Development and Integration of New Processes for Greenhouse Gases Management in Multi-Plant, Chemical Production Complexes

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A joint industry-university research effort

IMC Phosphates, Motiva Enterprises,

Louisiana State University, Lamar University

Sponsored by U. S. Environmental Protection Agency

NATO CCMS Pilot Study on Clean Products and Processes

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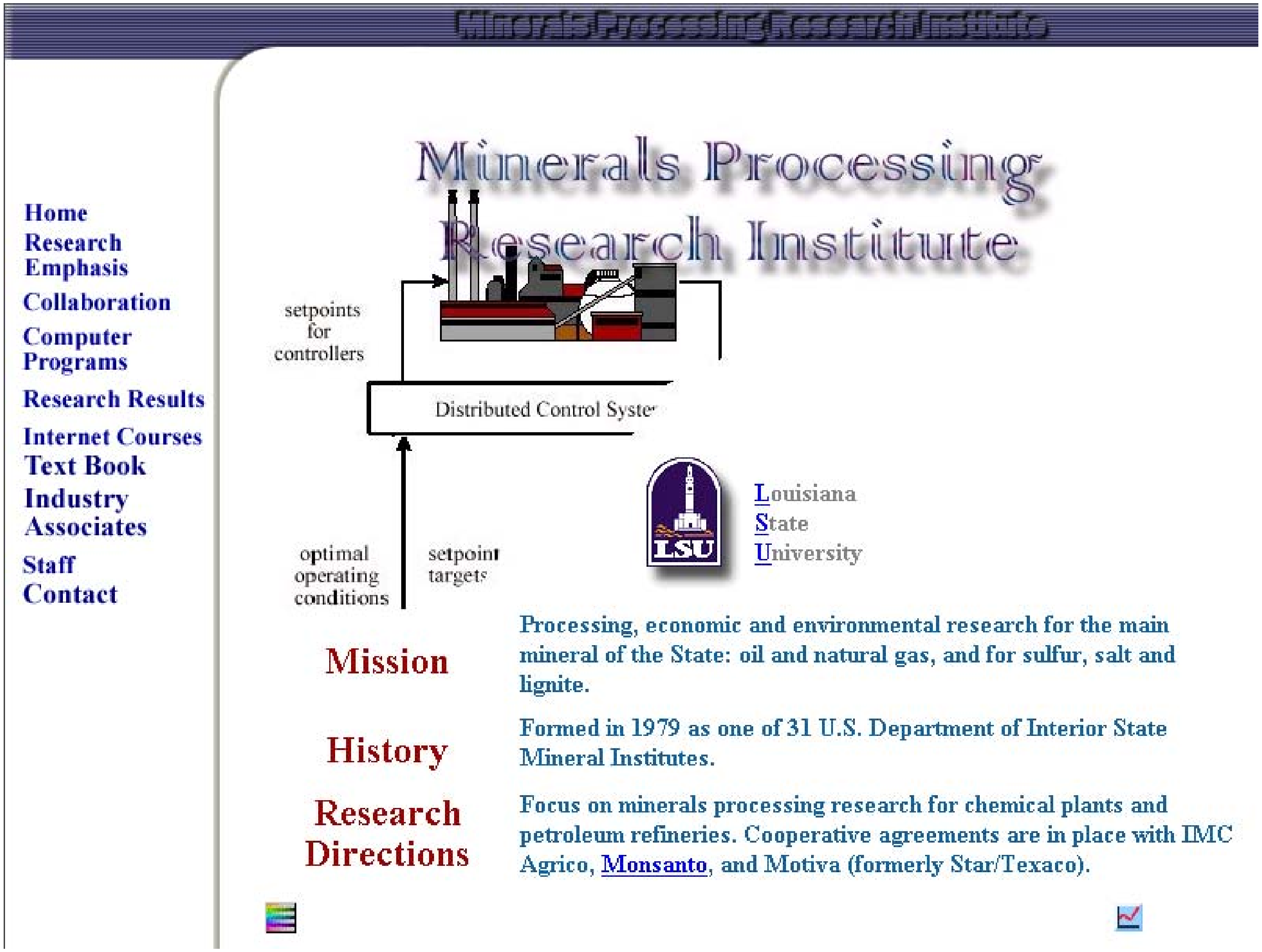
Hotel San Michele, Cetraro, Italy

LSU Mineral Processing Research Institute



All of the information given in this presentation is available at www.mpri.lsu.edu

Background

Pollution prevention
- was an environmental issue
- now a critical business opportunity

Long term cost of ownership must be evaluated with short term cash flows

Companies undergoing difficult institutional transformations
Emphasis on pollution prevention has broadened to include:

Total (full) cost accounting
Life cycle assessment
Sustainable development
Eco-efficiency (*eco*nomic and *eco*logical)

Broader Assessment of Current and Future Manufacturing in the Chemical Industry

Driving forces

- ISO 14000,
- "the polluter pays principle"
- Anticipated next round of Federal regulations associated with global warming
- Sustainable development

Sustainable development

- Concept that development should meet the needs of the present without sacrificing the ability of the future to meet its needs

Sustainable development costs - external costs

- Costs that are not paid directly
- Those borne by society
- Includes deterioration of the environment by pollution within compliance regulations.

Koyoto Protocol - annual limits on greenhouse gases proposed beginning in 2008 - 7% below 1990 levels for U.S.

Overview of Presentation

Chemical Complex and Cogeneration Analysis System

for multi-plant chemical production complexes

Advanced Process Analysis System

for operating plants

Chemical Complex and Cogeneration Analysis System

Objective: To give corporate engineering groups new capability to design:

- New processes for products from greenhouse gases
- Energy efficient and environmentally acceptable plants

Introduction

- Opportunities
  - Processes for conversion of greenhouse gases to valuable products
  - Cogeneration

- Methodology
  - Chemical Complex and Cogeneration Analysis System
  - Application to chemical complex in the lower Mississippi River corridor

Related Work and Programs

- Aspen Technology
- Department of Energy (DOE)
  www.oit.doe.gov/bestpractice
- Environmental Protection Agency (EPA)
  www.epa.gov/opptintr/greenengineering

Chemical Complex and Cogeneration Analysis System

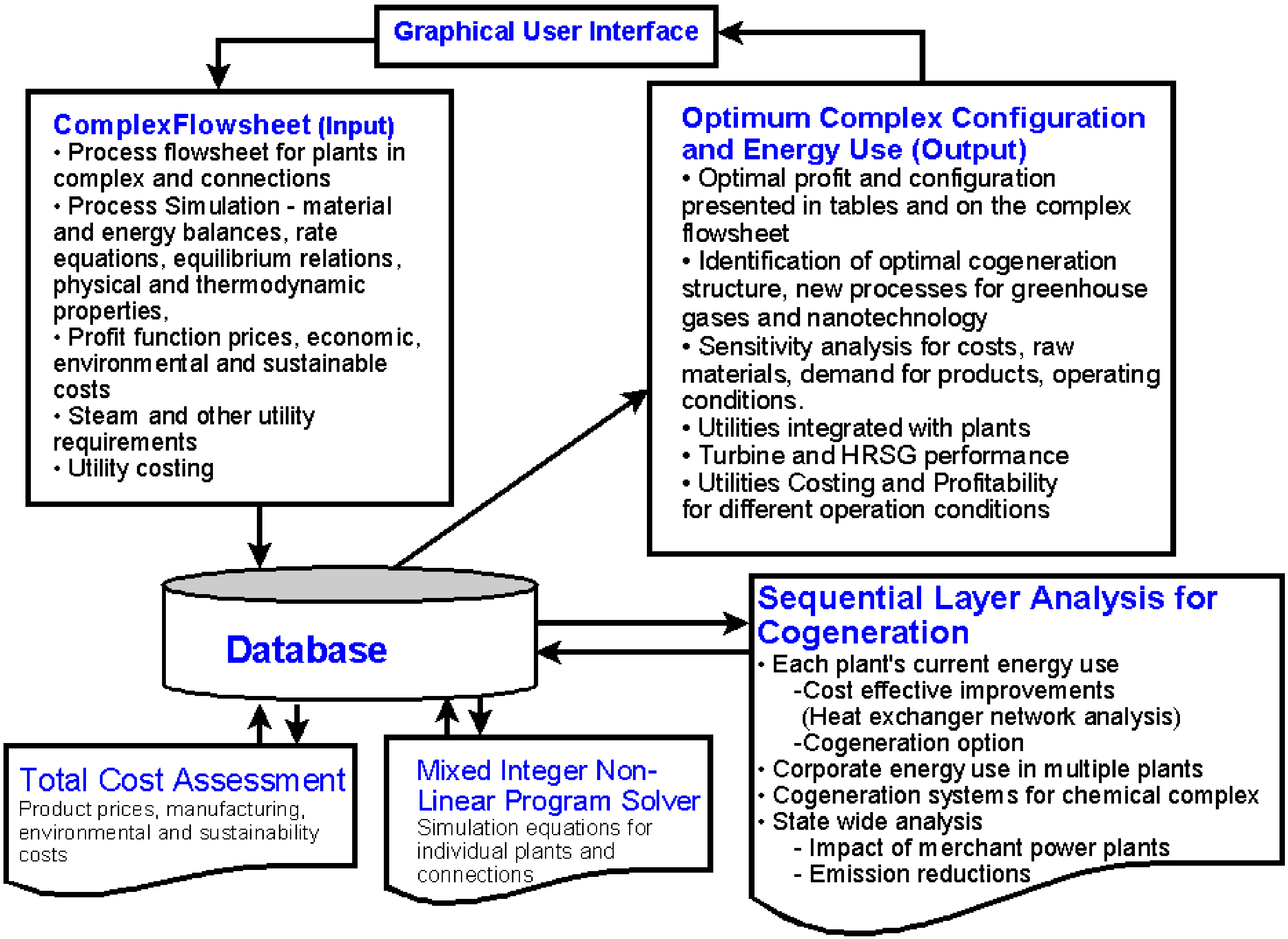
Chemical Complex Analysis System

Determines the best configuration of plants in a chemical complex based on the AIChE Total Cost Assessment (TCA) and incorporates EPA Pollution Index methodology (WAR) algorithm

Cogeneration Analysis System

Determines the best energy use based on economics, energy efficiency, regulatory emissions and environmental impacts from greenhouse gas emissions.

Structure of the System



AIChE Total Cost Assessment

-Includes five types of costs: I direct, II overhead, III liability, IV internal intangible, V external (borne by society - sustainable)

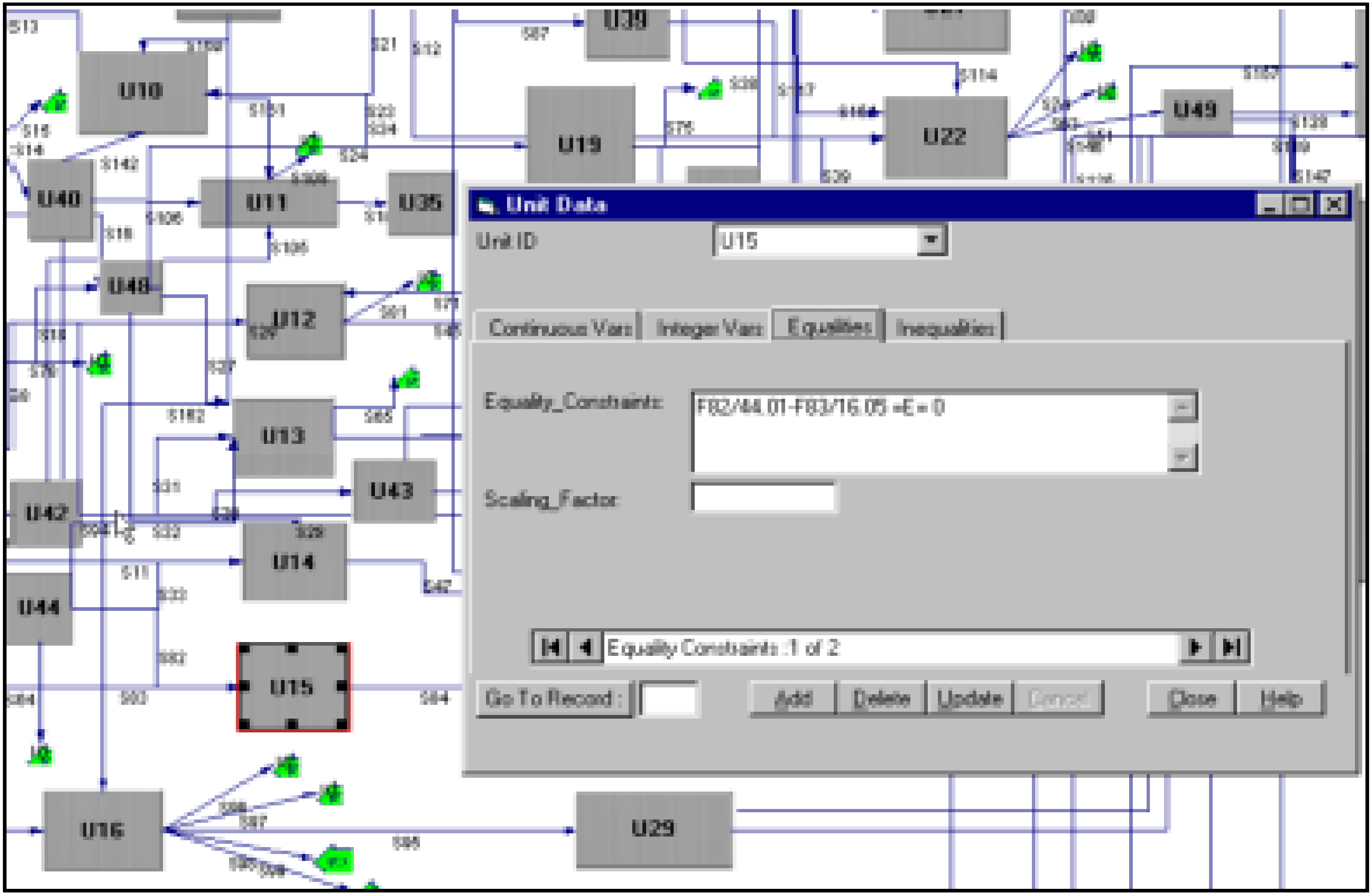
- Sustainable costs are costs to society from damage to the environment caused by emissions within regulations, e.g., sulfur dioxide 4.0 lb per ton of sulfuric acid produced
- Environmental costs – compliance, fines, 20% of manufacturing costs
- Combined five TCA costs into economic, environmental and sustainable costs

  economic – raw materials, utilities, etc

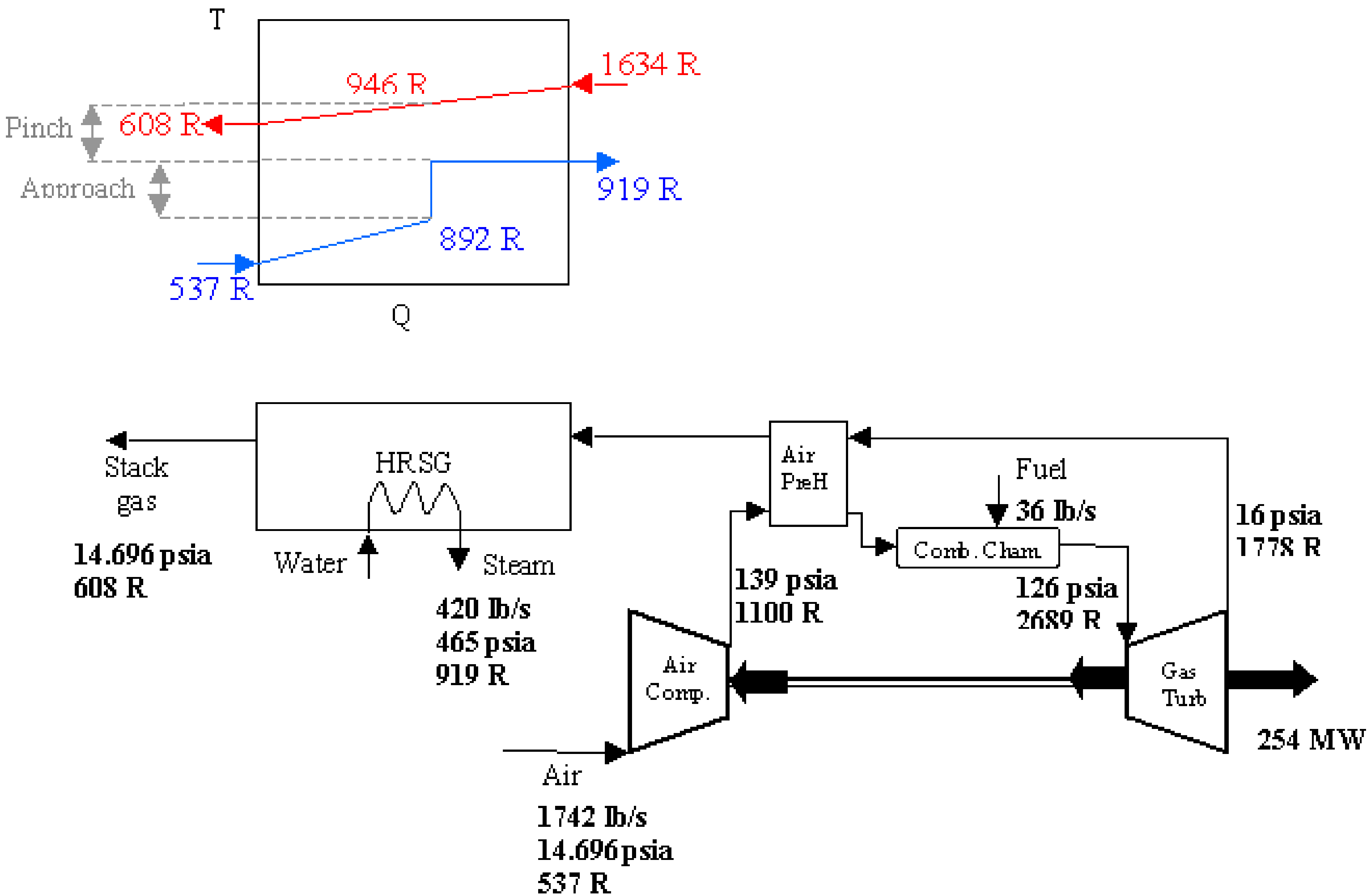
  environmental – 67% of raw materials

  sustainable – estimated from sources

Illustration of Input to the System for Unit Data



Typical Cogeneration Results on the CHP Diagram



Comparison of Power Generation

	Conventional	Cogeneration
Operating efficiency	33%	77%
Heat rate (BTU/kWh)	>10,000	5,000-6,000
NO_x emission (lbs of NO_x / MWh)	4.9	0.167
CO_2 emission (tons of CO_2 / MWh)	1.06	0.30

Plants in the lower Mississippi River Corridor

Saint Francisville
Crown Vantage

Port Hudson
Georgia-Pacific

North of Baton Rouge
Ferro (Grant)
Safety - Kleen (Laidlaw)
Exxon (Allied / Paxon)
Exxon Resins
Deltech (Foster Grant)
Exxon Plastics

Baton Rouge
Rhodia (Stauffer)
LaRoche (Kaiser)
DSM (Copolymer
Albemarle (Ethyl)
Formosa (Allied)
Exxon - Refinery
Exxon Chemical
Allied Signal

St Gabriel
Air Products
Novartis (Ciba Geigy)
Ciba
Pioneer (Stauffer)
ICI
Zeneca

Carville
Cosmar
Fina

Geismar
Borden
Air Liquide
Uniroyal
Rubicon
Praxair
BASF
Shell Chem
Air Prod
Vulcan

Geismar
Allied Signal
Williams (UTexas)
PCS Nitrogen
(Arcadian)
Rhodia

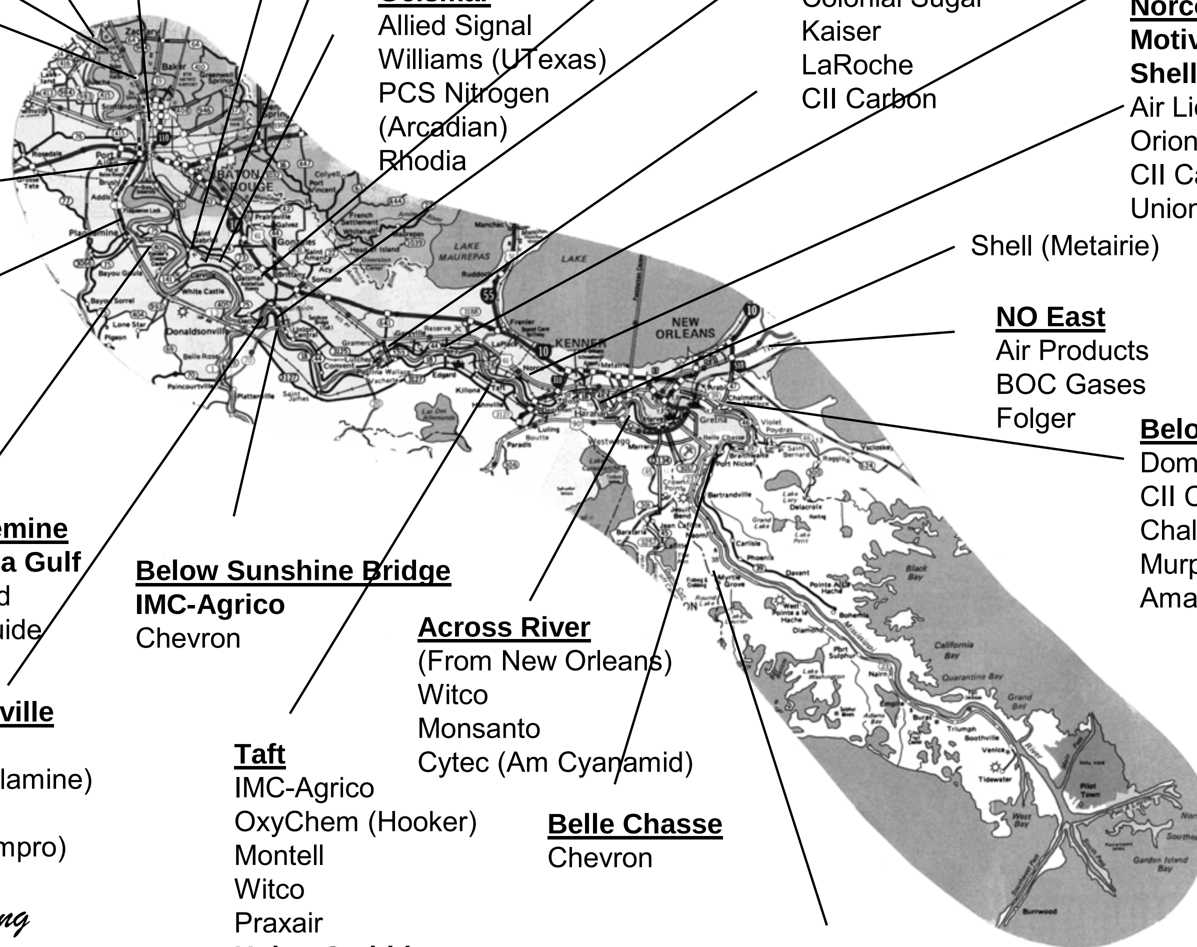
Sunshine Bridge & Below
Air Products
Motiva (Star/Texaco)
DuPont
OxyChem (Convent)
IMC - Agrico

Garyville
Nalco
Marathon
Epsilon
Betz (Reserve)
DuPont (LaPlace)

Gramercy
Colonial Sugar
Kaiser
LaRoche
CII Carbon

Norco
Motiva (Shell NMC)
Shell Chemical
Air Liquide
Orion (TransAmerican)
CII Carbon
Union Carbide

Shell (Metairie)



Port Allen
Placid
Exxon - Lubes

Addis / Plaquemine
Borden (OxyChem)
Sid Richardson
DSM Copolymer
Dow
Geon
Air Liquide
Air Products

Plaquemine
Georgia Gulf
Ashland
Air Liquide
Praxair

Donaldsonville
CF
Borden (Melamine)
Triad #1
Triad #2 (Ampro)

Below Sunshine Bridge
IMC-Agrico
Chevron

Taft
IMC-Agrico
OxyChem (Hooker)
Montell
Witco
Praxair
Union Carbide

Across River
(From New Orleans)
Witco
Monsanto
Cytec (Am Cyanamid)

Belle Chasse
Chevron

NO East
Air Products
BOC Gases
Folger

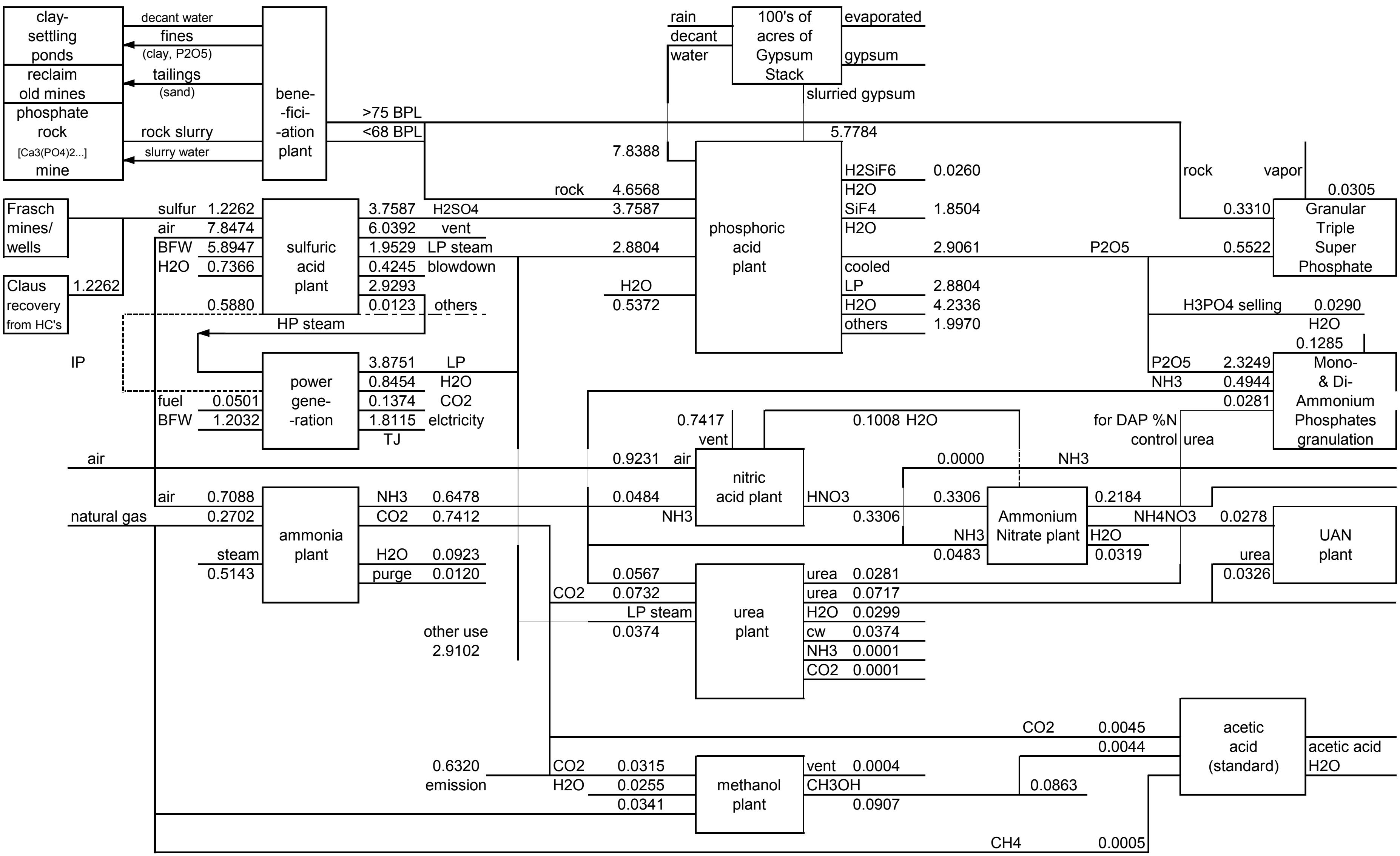
Below NO
Domino Sugar
CII Carbon
Chalmette Ref (Mobil)
Murphy
Amax

BP Amoco

son, R.W., 2000

Petrochemical Plants Along
The lower Mississippi River Corridor

Expanded Agricultural Chemical Complex

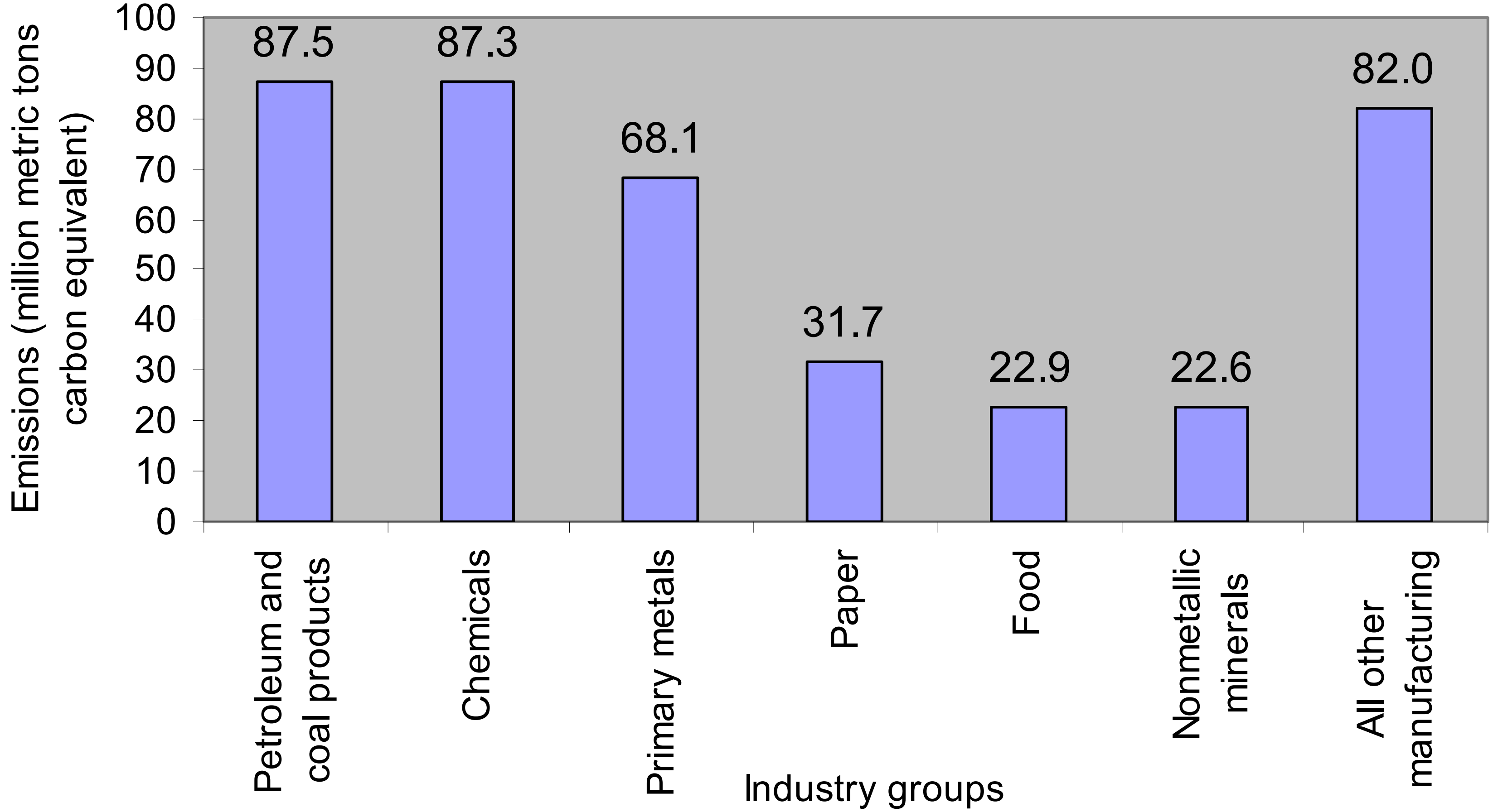


Plants in the lower Mississippi River Corridor, Base Case. Flow Rates in Million Tons Per Year

Some Chemical Complexes in the World

Continent	Name and Site	Notes
North America	•Gulf coast petrochemical complex in Houston area (U.S.A.) and •Chemical complex in the Baton Rouge-New Orleans Mississippi River Corridor (U.S.A.)	•Largest petrochemical complex in the world, supplying nearly two-thirds of the nation’s petrochemical needs
South America	•Petrochemical district of Camacari-Bahia (Brazil) •Petrochemical complex in Bahia Blanca (Argentina)	•Largest petrochemical complex in the southern hemisphere
Europe	•Antwerp port area (Belgium) •BASF in Ludwigshafen (Germany)	•Largest petrochemical complex in Europe and world wide second only to Houston, Texas •Europe’s largest chemical factory complex
Asia	•The Singapore petrochemical complex in Jurong Island (Singapore) •Petrochemical complex of Daqing Oilfield Company Limited (China) •SINOPEC Shanghai Petrochemical Co. Ltd. (China) •Joint-venture of SINOPEC and BP in Shanghai under construction (2005) (China) •Jamnagar refinery and petrochemical complex (India) •Sabic company based in Jubail Industrial City (Saudi Arabia) •Petrochemical complex in Yanbu (Saudi Arabia) •Equate (Kuwait)	•World’s third largest oil refinery center •Largest petrochemical complex in Asia •World’s largest polyethylene manufacturing site •World’s largest & most modern for producing ethylene glycol and polyethylene
Oceania	•Petrochemical complex at Altona (Australia) •Petrochemical complex at Botany (Australia)	
Africa	petrochemical industries complex at Ras El Anouf (Libya)	one of the largest oil complexes in Africa

CO_2 Emissions from Industries



Total Energy-Related Carbon Dioxide Emissions for Selected Manufacturing Industries, 1998, from EIA, 2001

Carbon Dioxide Emissions and Utilization

(Million Metric Tons Carbon Equivalent Per Year)

CO_2 emissions and utilization		Reference
Total CO_2 added to atmosphere		IPCC (1995)
Burning fossil fuels	5,500	
Deforestation	1,600	
Total worldwide CO_2 from consumption and flaring of fossil fuels		EIA (2002)
United States	1,526	
China	792	
Russia	440	
Japan	307	
All others	3,258	
U.S. CO_2 emissions		Stringer (2001)
Industry	630	
Buildings	524	
Transportation	473	
Total	1,627	
U.S. industry (manufacturing)		EIA (2001)
Petroleum, coal products and chemicals	175	
Chemical and refinery (BP)		McMahon (1999)
Combustion and flaring	97%	
Noncombustion direct CO_2 emission	3%	
Agricultural chemical complex in the lower Mississippi River corridor excess high purity CO_2	0.183	Hertwig et al. (2002)
CO_2 used in chemical synthesis	30	Arakawa et al. (2001)

Commercial Uses of CO_2

- 110 million tons of CO_2 for chemical synthesis
  - Urea (chiefly, 90 million ton of CO_2)
  - Methanol (1.7 million tons of CO_2)
  - Polycarbonates
  - Cyclic carbonates
  - Salicylic acid
  - Metal carbonates

Surplus Carbon Dioxide

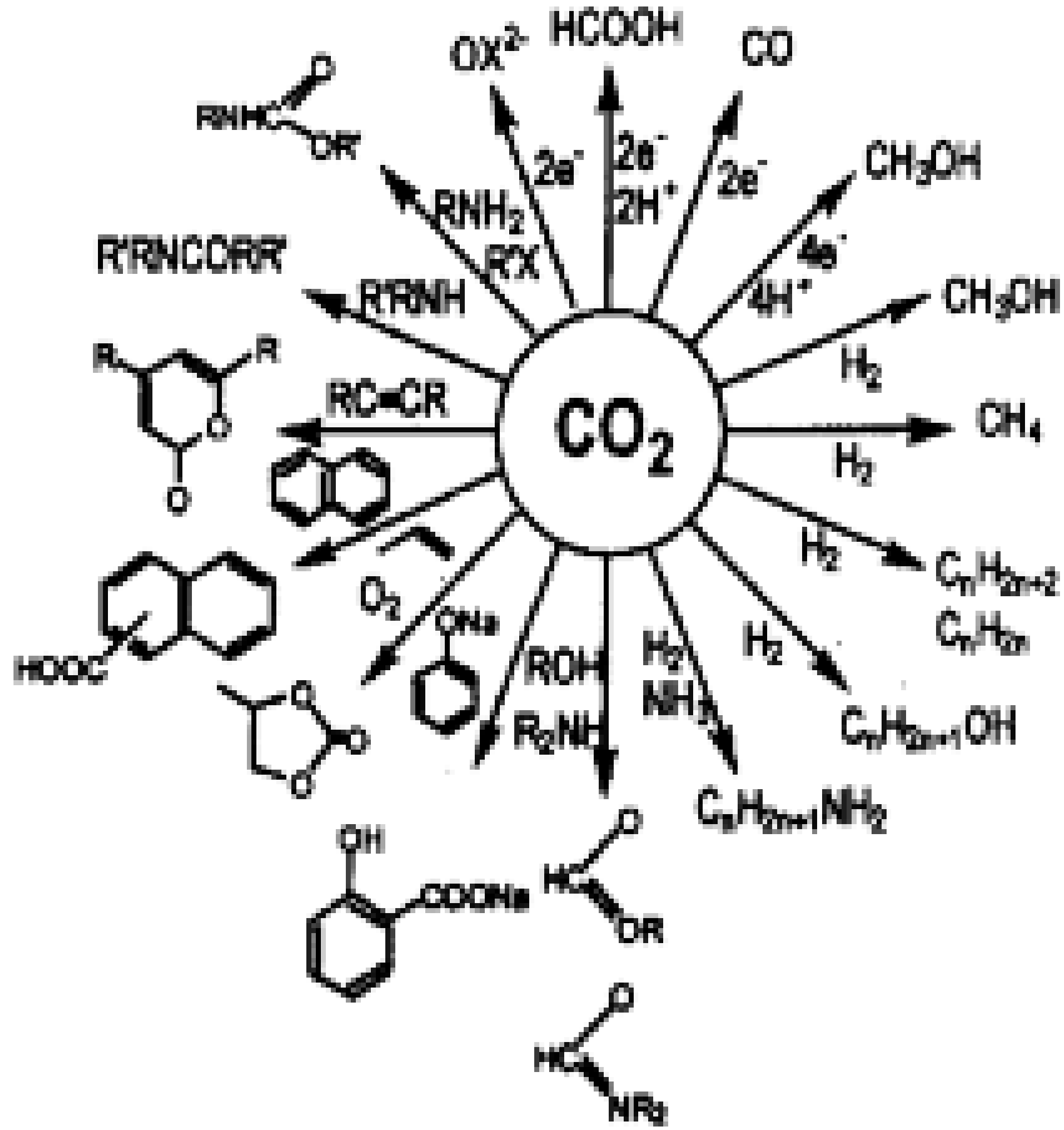
Ammonia plants produce 1.2 million tons per year in lower Mississippi River corridor

Methanol and urea plants consume 0.15 million tons per year

Surplus high-purity carbon dioxide 1.0 million tons per year vented to atmosphere

Greenhouse Gases as Raw Material

- Intermediate of fine chemicals for the chemical industry
  -C(O)O-: Acids, esters, lactones
  -O-C(O)O-:Carbonates
  -NC(O)OR-: Carbamic esters
  -NCO: Isocyanates
  -N-C(O)-N: Ureas
- Use as a solvent
- Energy rich products
  CO, CH_3OH



From Creutz and Fujita, 2000

Catalytic Reactions of CO_2 from Various Sources

Hydrogenation

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ methanol

$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O$ ethanol

$CO_2 + H_2 \rightarrow CH_3\text{-}O\text{-}CH_3$ dimethyl ether

Hydrolysis and Photocatalytic Reduction

$CO_2 + 2H_2O \rightarrow CH_3OH + O_2$

$CO_2 + H_2O \rightarrow HC{=}O\text{-}OH + 1/2O_2$

$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$

Hydrocarbon Synthesis

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ methane and higher HC

$2CO_2 + 6H_2 \rightarrow C_2H_4 + 4H_2O$ ethylene and higher olefins

Carboxylic Acid Synthesis

$CO_2 + H_2 \rightarrow HC{=}O\text{-}OH$ formic acid

$CO_2 + CH_4 \rightarrow CH_3\text{-}C{=}O\text{-}OH$ acetic acid

Other Reactions

CO_2 + ethylbenzene $\rightarrow$ styrene

$CO_2 + C_3H_8 \rightarrow C_3H_6 + H_2 + CO$
dehydrogenation of propane

$CO_2 + CH_4 \rightarrow 2CO + H_2$ reforming

Graphite Synthesis

$CO_2 + H_2 \rightarrow C + H_2O$

$CH_4 \rightarrow C + H_2$
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

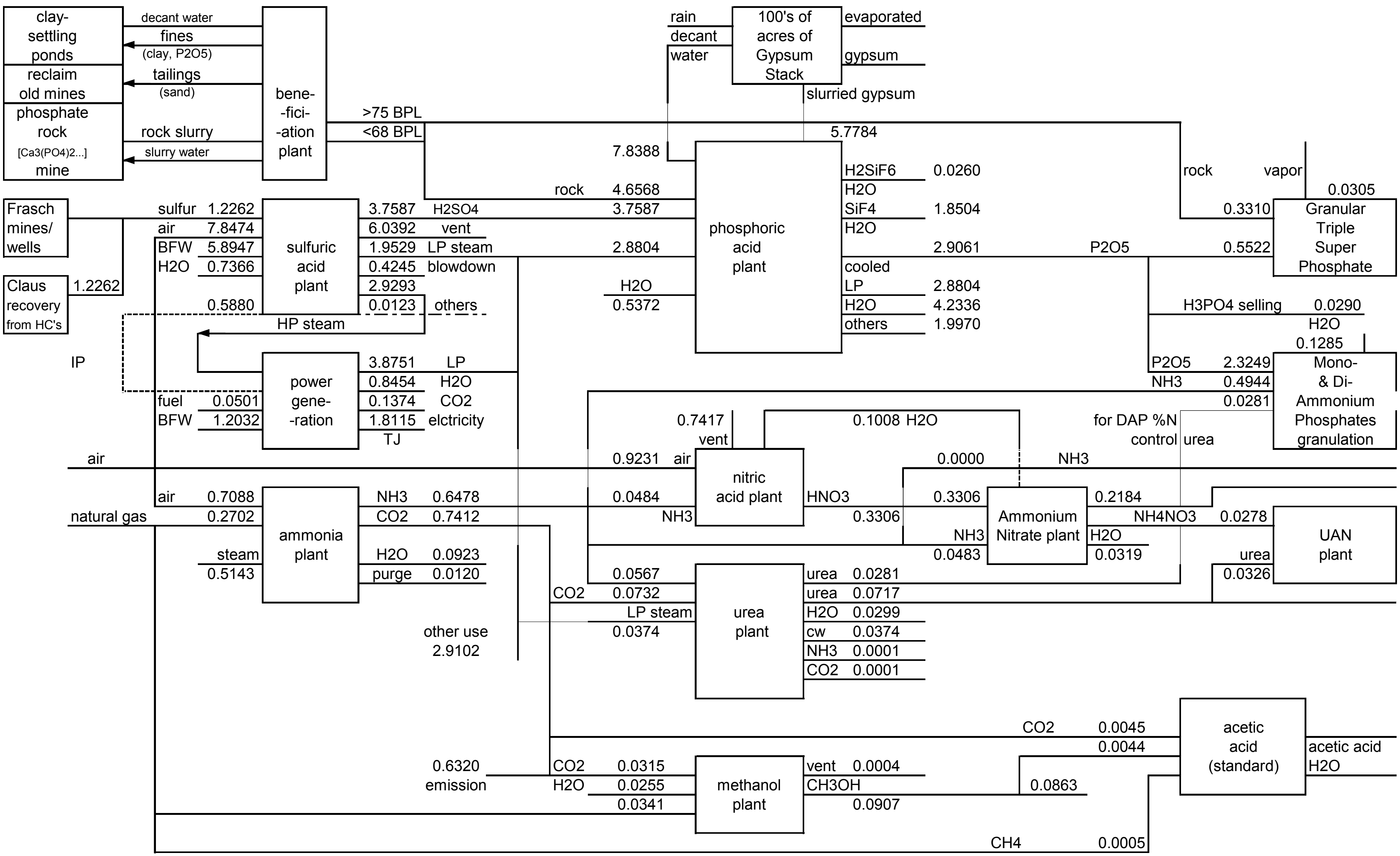
Amine Synthesis

$CO_2 + 3H_2 + NH_3 \rightarrow CH_3\text{-}NH_2 + 2H_2O$ methyl amine and higher amines

Application of the System to Chemical Complex in the Lower Mississippi River Corridor

- Base case
- Superstructure
- Optimal structure

Base Case of Actual Plants

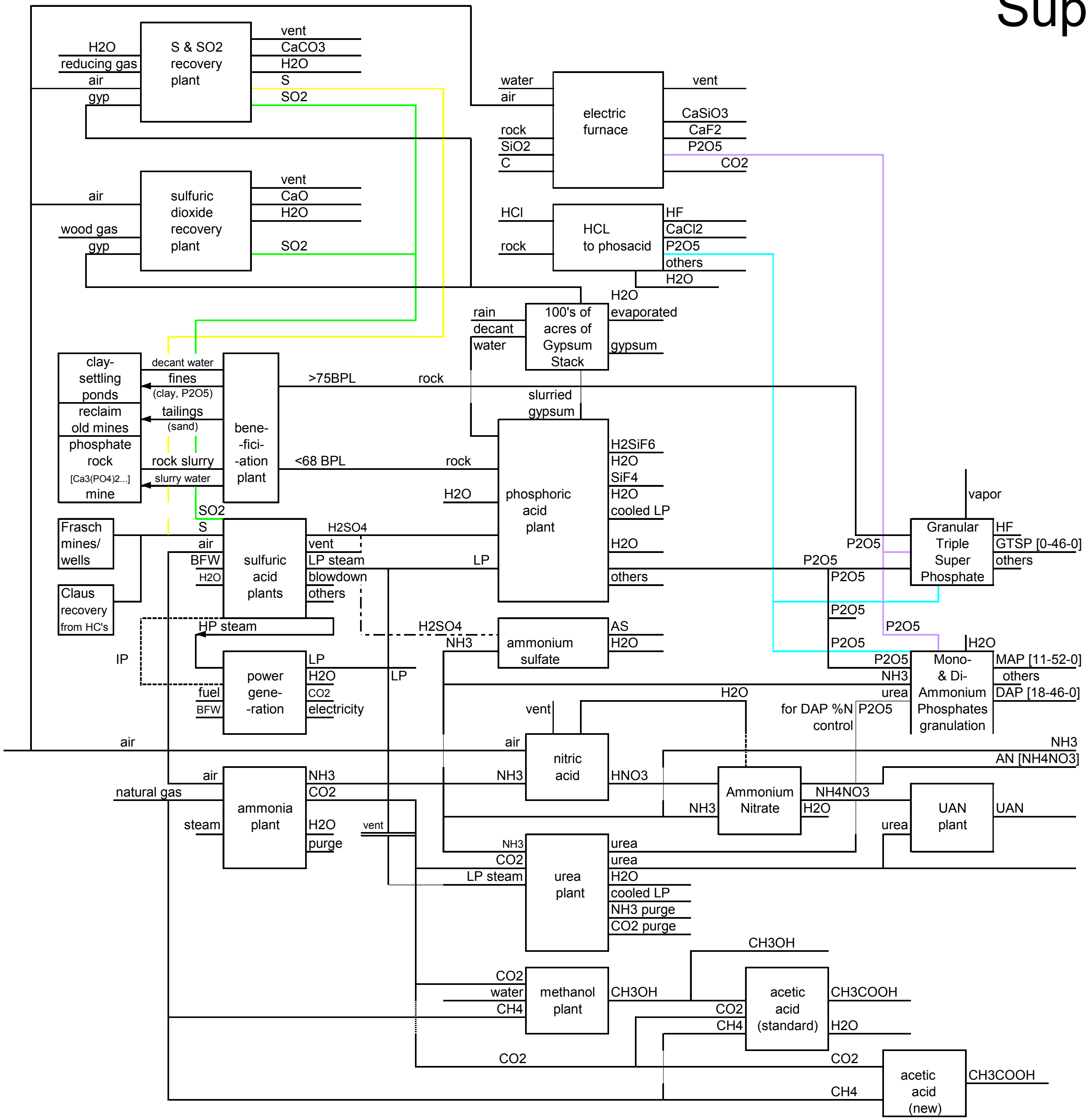


Plants in the lower Mississippi River Corridor, Base Case. Flow Rates in Million Tons Per Year

Processes in the Superstructure

Processes in Superstructure	
Processes in Base Case	Electric furnace process for phosphoric acid HCl process for phosphoric acid Ammonium sulfate SO_2 recovery from gypsum process S & SO_2 recovery from gypsum process Acetic acid – new CO2-CH4 catalytic process
Ammonia Nitric acid Ammonium nitrate Urea UAN Methanol Granular triple super phosphate MAP & DAP Power generation Contact process for Sulfuric acid Wet process for phosphoric acid Acetic acid-conventional process	

Superstructure



Superstructure Characteristics

Options

- Three options for producing phosphoric acid
- Two options for producing acetic acid
- One option for sulfuric acid
- Two options for recover sulfur and sulfur dioxide
- New plants for
  - ammonium sulfate
  - recover sulfur and sulfur dioxide

Mixed Integer Nonlinear Program

594 continuous variables

7 integer variables

505 equality constraint equations
for material and energy balances

27 inequality constraints for availability of raw materials
demand for product, capacities of the plants in the complex

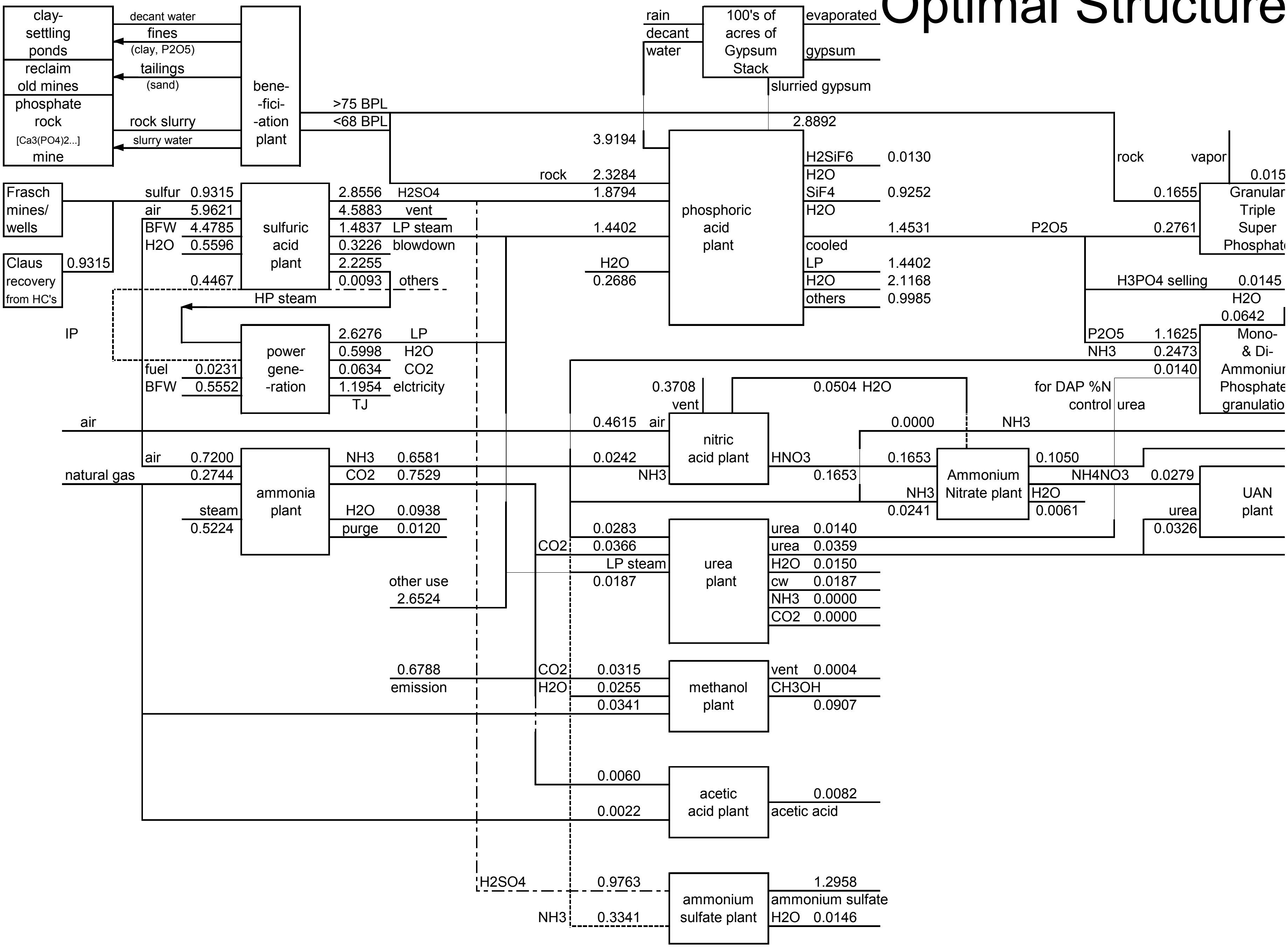
Raw Material and Product Prices

Raw Materials	Cost ($/mt)
Natural Gas	245
Phosphate Rock	
wet process	27
electrofurnace	24
HCl process	25
GTSP process	30
HCl	50
Sulfur	
Frasch	42
Claus	38
C electrofurnace	760

Raw Materials	Cost ($/mt)
Market cost for short term purchase	
Reducing gas	1394
Wood gas	634
Sustainable Costs and Credits	
Credit for CO_2 Consumption	6.50
Debit for CO_2 Production	3.25
Credit for HP Steam	10
Credit for IP Steam	6.4
Credit for gypsum Consumption	5
Debit for gypsum Production	2.5
Debit for NO_x Production	1025

Products	Price ($/mt)
Ammonia	190
Methanol	96
Acetic Acid	623
GTSP	142
MAP	180
DAP	165
NH_4NO_3	153
UAN	112
Urea	154
H_3PO_4	320
$(NH_4)_2SO_4$	187

Optimal Structure



Comparison of Base Case and Optimal Structure

		Base case		Optimal structure	
Profit (U.S.$/year)		148,087,243		246,927,825	
Environmental cost (U.S.$/year)		179,481,000		123,352,900	
Sustainability cost (U.S.$/year)		-17,780,800	energy	-16,148,900	energy
Plant name	Capacity (mt/year)	Capacity	requirement	Capacity	requirement
	(upper-lower bounds)	(mt/year)	(TJ/year)	(mt/year)	(TJ/year)
Ammonia	329,030-658,061	647,834	3,774	658,061	3,834
Nitric acid	0-178,547	178,525	-649	89,262	-324
Ammonium nitrate	113,398-226,796	226,796	116	113,398	26
Urea	49,895-99,790	99,790	127	49,895	63
Methanol	90,718-181,437	90,719	1,083	90,719	1,083
UAN	30,240-60,480	60,480	0	60,480	0
MAP	0-321,920	321,912		160,959	
DAP	0-2,062,100	2,062,100	2,127	1,031,071	1,063
GTSP	0-822,300	822,284	1,036	411,150	518
Contact process sulfuric acid	1,851,186-3,702,372	3,702,297	-14,963	2,812,817	-11,368
Wet process phosphoric acid	697,489-1,394,978	1,394,950	7,404	697,489	3,702
Electric furnace phosphoric acid	697,489-1,394,978	na	na	0	0
HCl to phosphoric acid	697,489-1,394,978	na	na	0	0
Ammonium sulfate	0-2,839,000	na	na	1,295,770	726
Acetic acid (standard)	0-8,165	8,165	268	0	0
Acetic acid (new)	0-8,165	na	na	8,165	92
SO2 recovery from gypsum	0-1,804,417	na	na	0	0
S & SO2 recovery from gypsum	0-903,053	na	na	0	0
Ammonia sale		0		0	
Ammnium Nitrate sale		218,441		105,043	
Urea sale		39,076		3,223	
Wet process phosphoric acid sale		13,950		6,975	
Methanol sale		86,361		90,719	
Total energy requirement from fuel gas			2,912		1,344

Comparison of Acetic Acid Processes

Process	Conventional Process	New Catalytic Process
Raw Materials	Methanol, Carbon Monoxide	Methane, Carbon Dioxide
Reaction Condition	450K, 30bar	350K, 25bar
Conversion of methane	100%	97%
Equipment	reactor, flash drum, four distillation columns	reactor, distillation column

Production Costs for Acetic Acid

Moulijn, et al., 2001

Plant Production Cost, (cents per kg)	Methanol Carbon Monoxide	Methane Carbon Dioxide
Raw materials	21.6	21.6
Utilities	3.3	1.7
Labor	1.2	1.2
Other (capital, catalyst)	10.1	10.1
Total Production Cost	36.2	34.6

Current market price 79 cents per kg

Catalytic Process for Acetic Acid

Capacity: 100 million pound per year of acetic acid

36,700 tons per year of carbon dioxide raw material

Potential Savings

Reduction in utilities costs for process steam $750,000

Energy savings from not having to produce this steam

275 trillion BTUs per year

Reduction in NOx emissions base on steam and power generation by cogeneration

3.5 tons per year

Reduction in carbon dioxide emissions

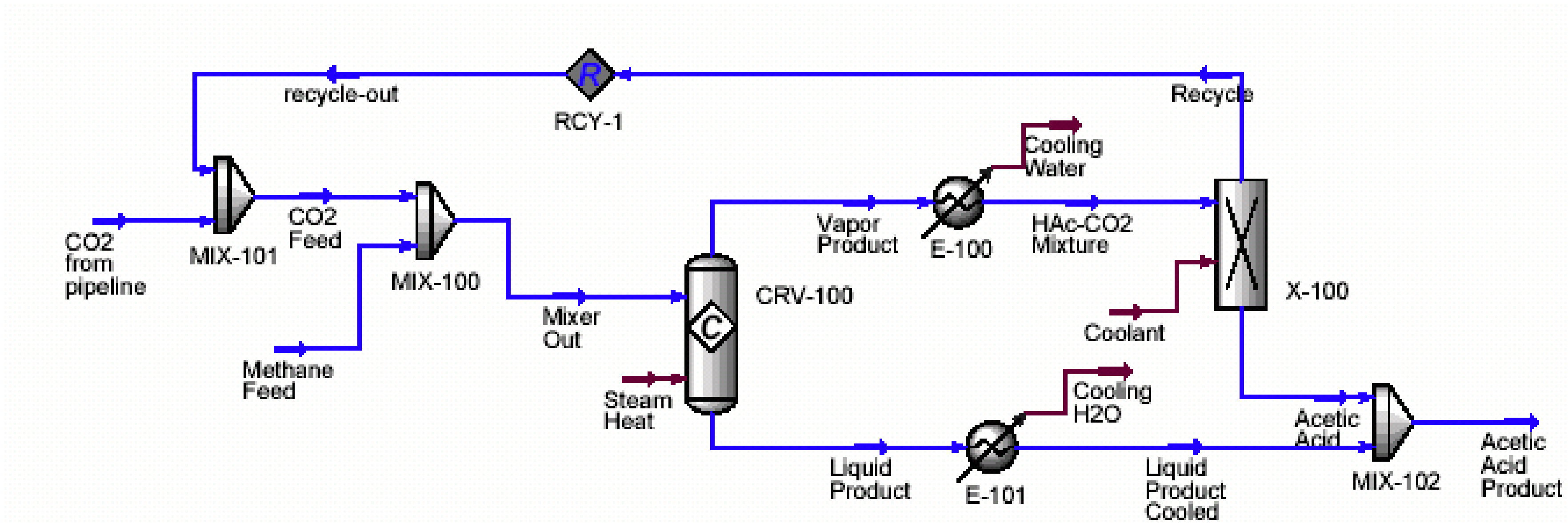
12,600 tons per year from the steam production

36,700 tons per year conversion to a useful product

Develop Process Information for the System

- Simulate process using HYSYS and Advanced Process Analysis System.
- Estimate utilities required.
- Perform economic analysis.
- Obtain process constraint equations from HYSIS and Advanced Process Analysis System.
- Maximize the profit function to find the optimum process configuration with the System.
- Incorporate into superstructure.

HYSYS Process Flow Diagram for Acetic Acid Process



Advanced Process Analysis System

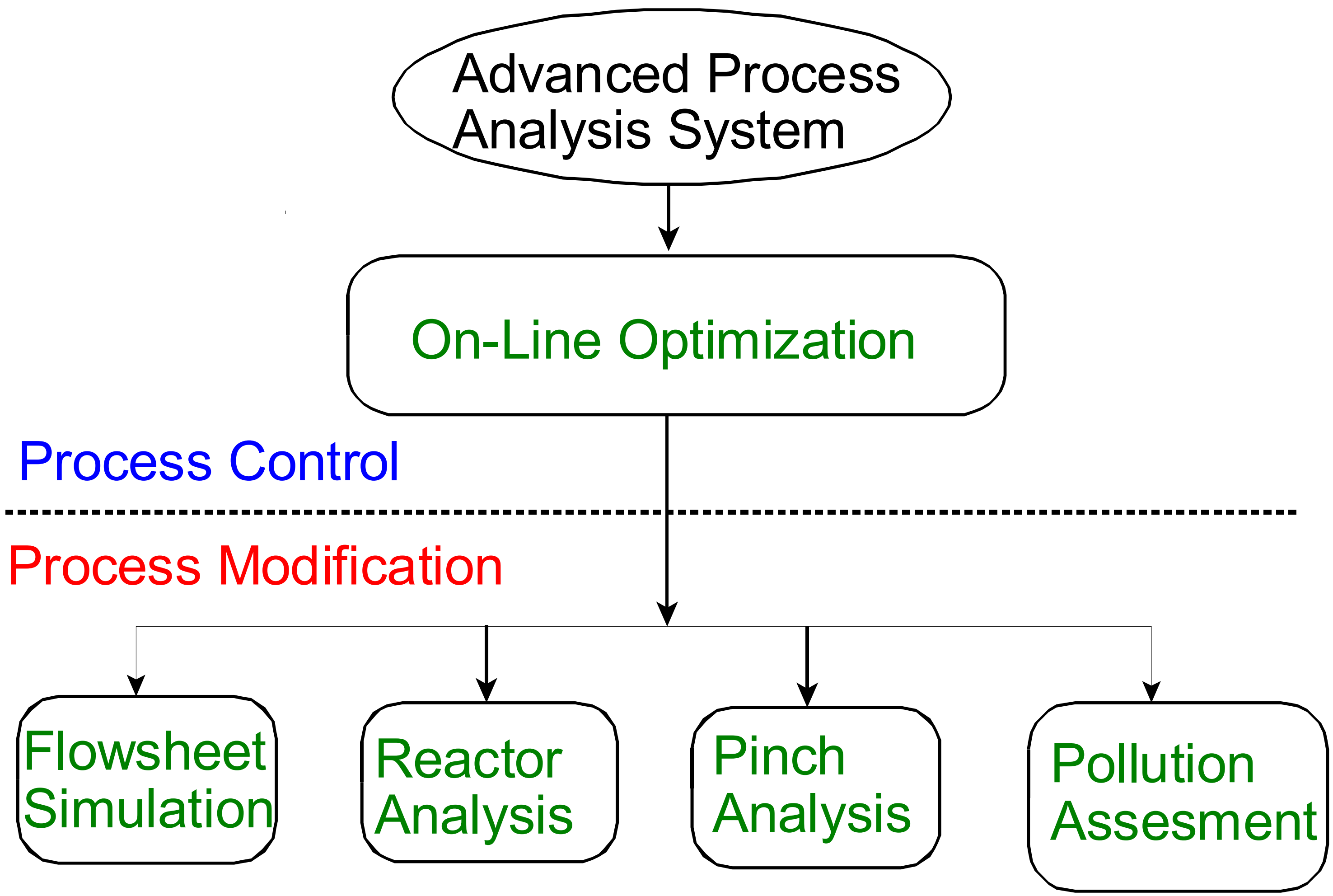
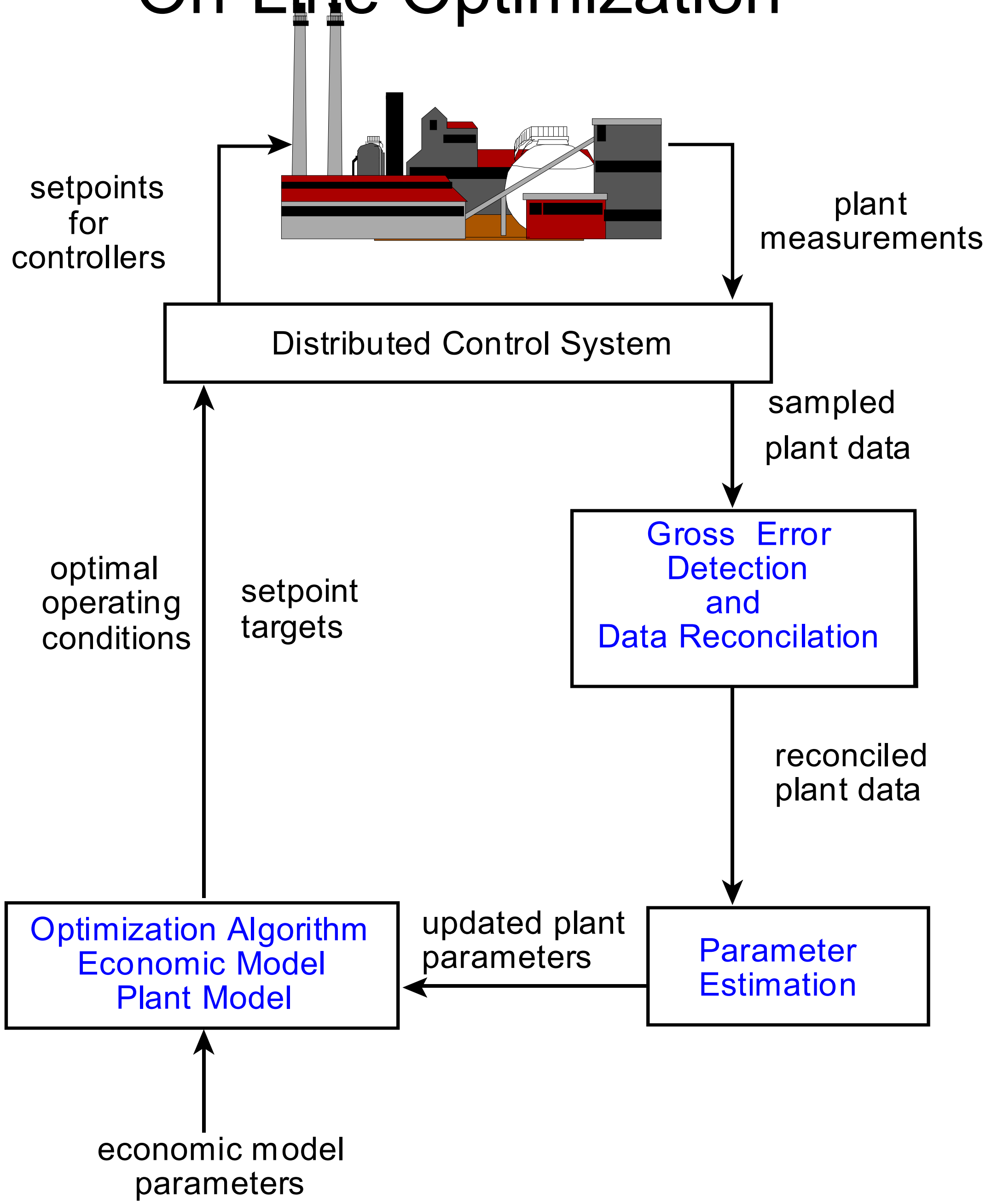
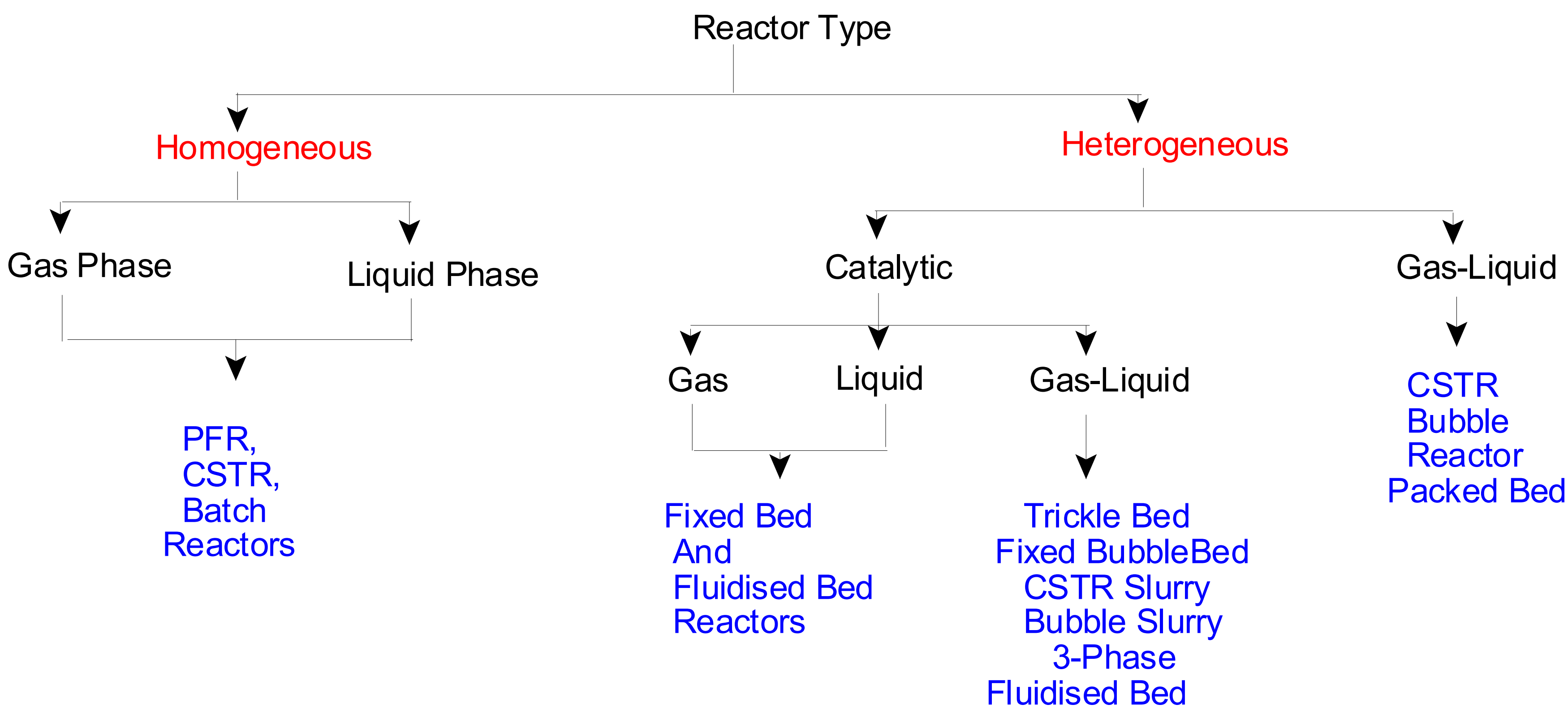


Fig. 1 Overview of Advanced Process Analysis System

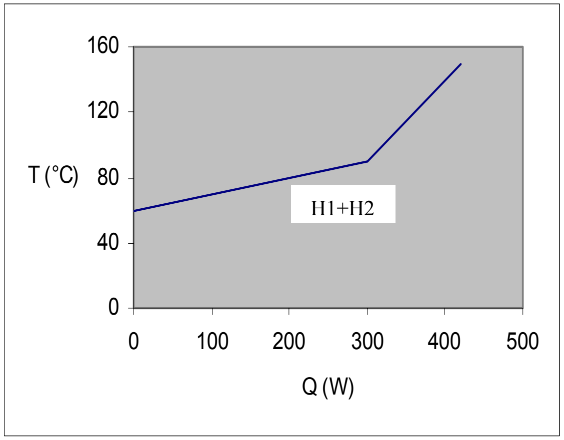
On-Line Optimization

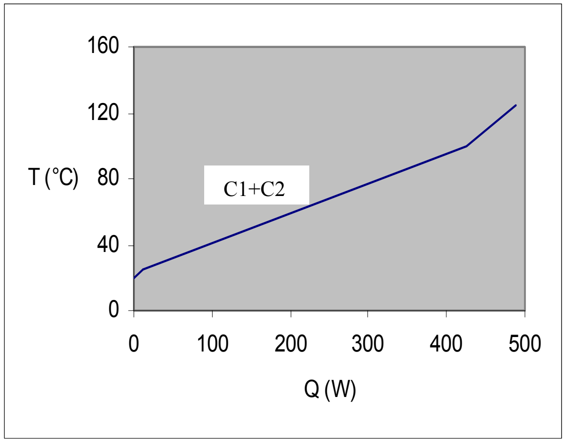


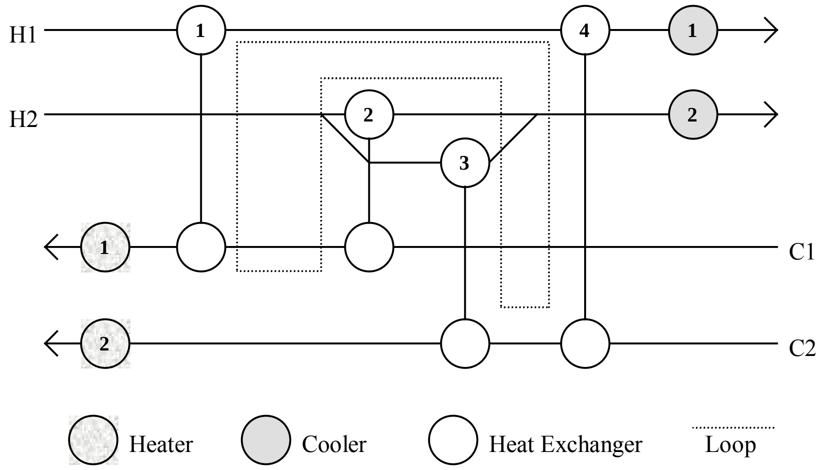
Reactor Analysis



Energy Integration – Pinch Analysis







Pollution Assessment

Waste Reduction Algorithm (WAR) and

Environmental Impact Theory

Pollution Index

I = wastes/products = - (ΣOut + ΣFugitive) / ΣP_n

Potential Environmental Impact

$$\Psi_k = \sum_l \alpha_l \Psi^s_{k,l}$$

α_l relative weighting factor

$\Psi^s_{k,l}$ units of potential environmental impact/mass of chemical k

Conclusions

- The System has been applied to an extended agricultural chemical complex in the lower Mississippi River corridor

- Economic model incorporated economic, environmental and sustainable costs.

- An optimum configuration of plants was determined with increased profit and reduced energy and emissions

- For acetic acid production, new catalytic process is better than conventional process based on energy savings and the reduction of NO_x and CO_2 emissions.

Conclusions

- Based on these results, the methodology could be applied to other chemical complexes in the world for reduced emissions and energy savings.

- The System includes the program with users manuals and tutorials. These can be downloaded at no cost from the LSU Mineral Processing Research Institute's web site www.mpri.lsu.edu

Future Work

- Add new processes for carbon dioxide

- Expand to a petrochemical complex in the lower Mississippi River corridor

- Add processes that produce fullerines and carbon nanotubes

Advanced Process Analysis System

On-Line Optimization and Flowsheet Simulation
- accurate description of the plant
- maintain optimum operating conditions

Pinch Analysis
- minimum utilities, steam and cooling water

Chemical Reactor Analysis
- select best chemical reactor from options

Pollution Assessment – WAR Algorithm
- identify sources of pollutant generation in the plant and process modifications

Advanced Process Analysis System

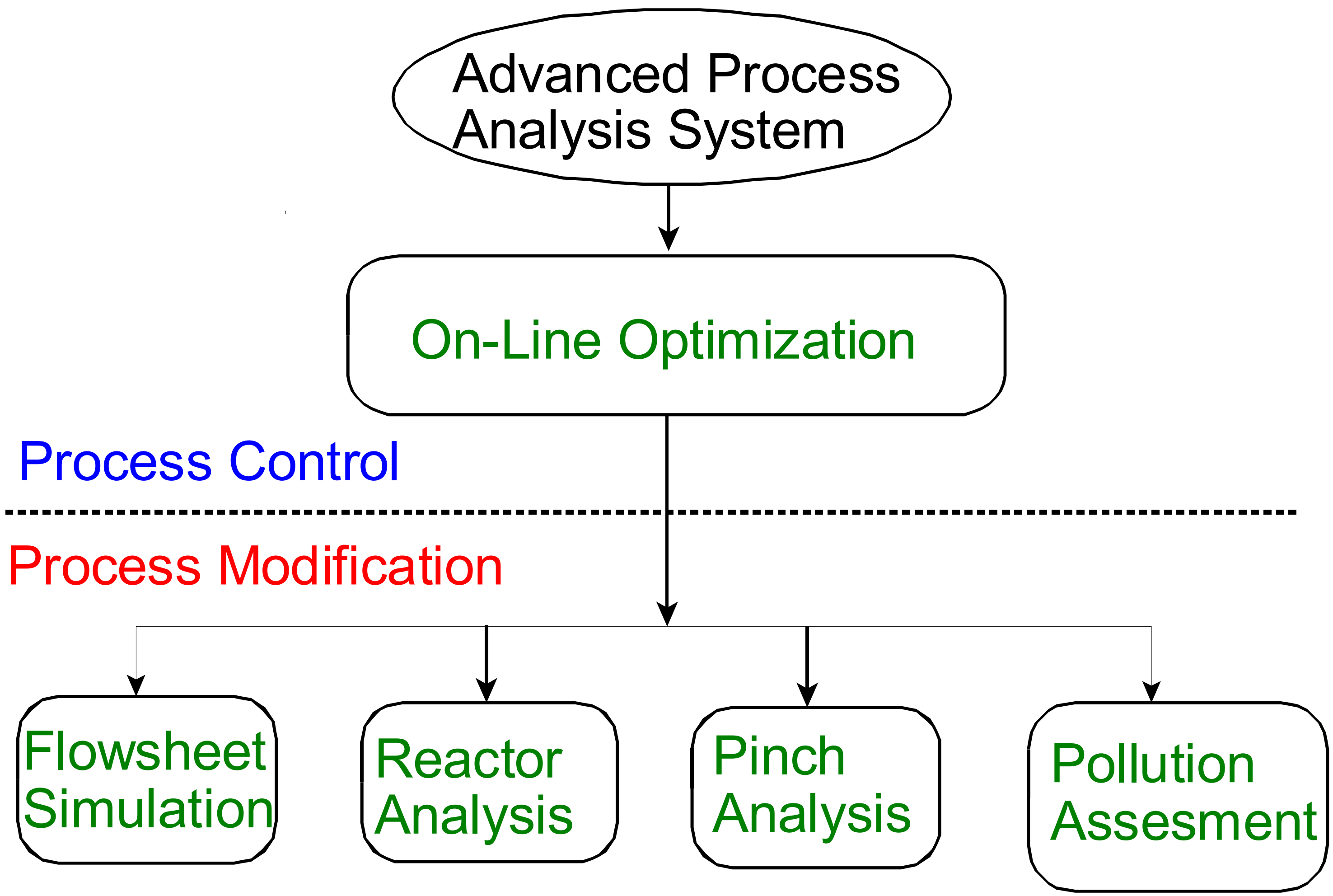


Fig. 1 Overview of Advanced Process Analysis System

Advanced Process Analysis System Structure

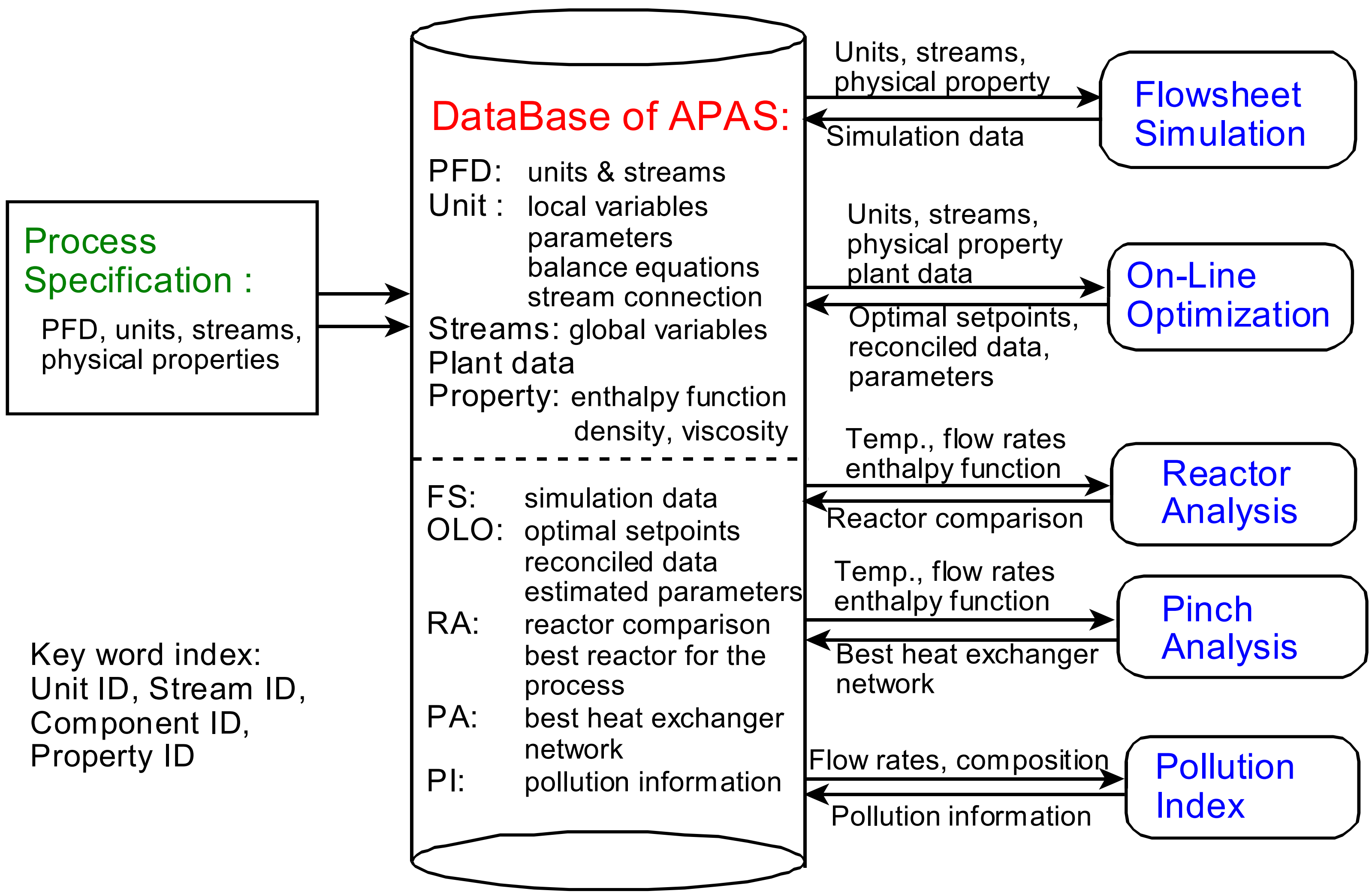


Fig. 2 Database Structure of Advanced Process Analysis System

On-Line Optimization

Automatically adjust operating conditions
with the plant's distributed control system

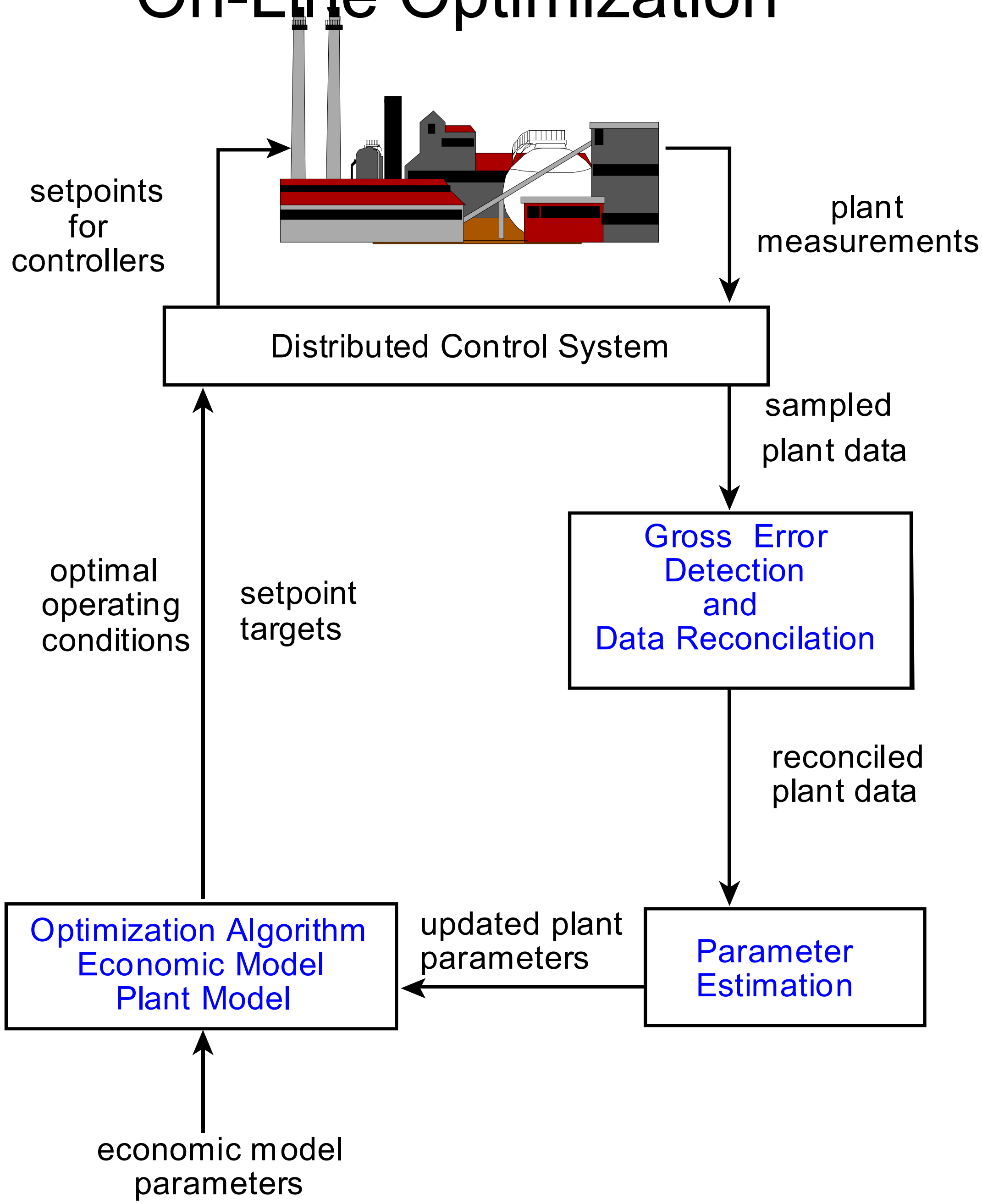
Maintains operations at optimal set points

Requires the solution of three NLP's
- gross error detection and data reconciliation
- parameter estimation
- economic optimization

BENEFITS

Improves plant profit by 3-5%
Waste generation and energy use are reduced
Increased understanding of plant operations

On-Line Optimization



Some Companies Using On-Line Optimization

United States
Texaco
Amoco
Conoco
Lyondel
Sunoco
Phillips
Marathon
Dow
Chevron
Pyrotec/KTI
NOVA Chemicals (Canada)
British Petroleum

Europe
OMV Deutschland
Dow Benelux
Shell
OEMV
Penex
Borealis AB
DSM-Hydrocarbons

Applications
mainly crude units in refineries and ethylene plants

Companies Providing On-Line Optimization

Aspen Technology - Aspen Plus On-Line
- DMC Corporation
- Setpoint
- Hyprotech Ltd.

Simulation Science - ROM
- Shell - Romeo

Profimatics - On-Opt
- Honeywell

Litwin Process Automation - FACS

DOT Products, Inc. - NOVA

On-Line Optimization Problem Size

	Contact	Alkylation	Ethylene
Units	14	76	-
Streams	35	110	~4,000
Constraints			
Equality	761	1579	~400,000
Inequality	28	50	~10,000
Variables			
Measured	43	125	~300
Unmeasured	732	1509	~10,000
Parameters	11	64	~100

Key Elements

Gross Error Detection

Data Reconciliation

Parameter Estimation

Economic Model
(Profit Function)

Plant Model
(Process Simulation)

Optimization Algorithm

Status of Industrial Practice for On-Line Optimization

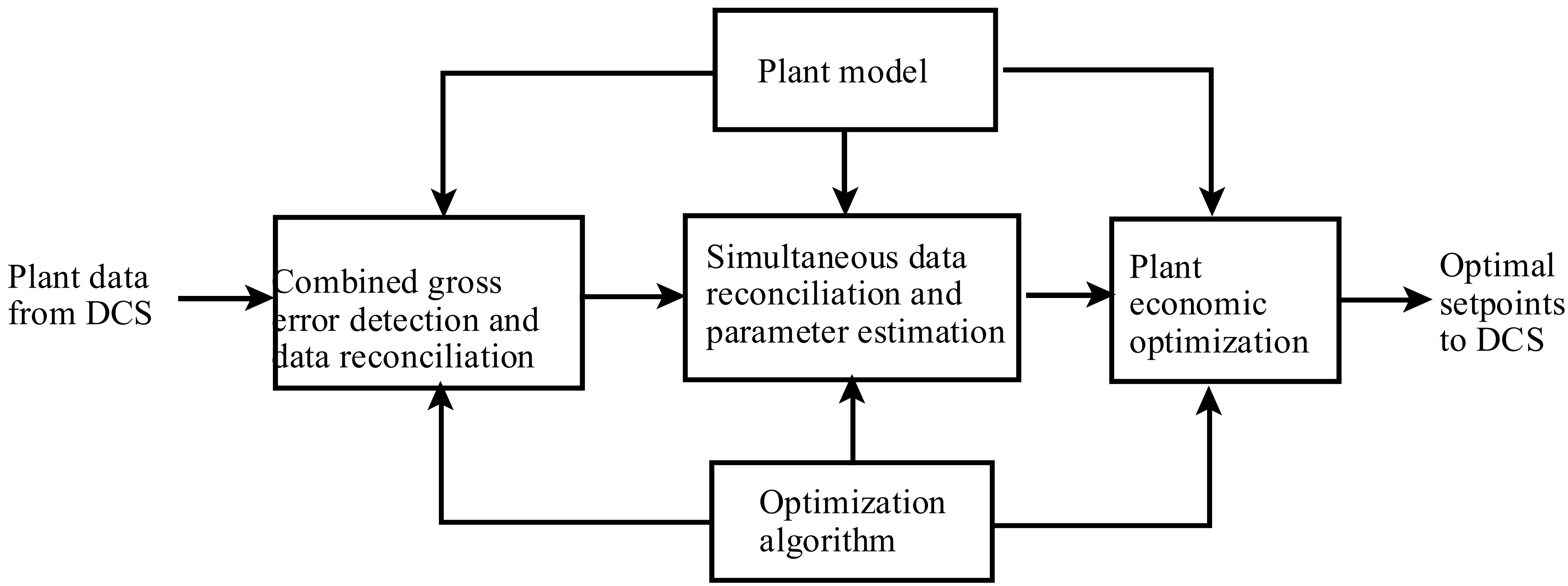
Steady state detection by time series screening

Gross error detection by time series screening

Data reconciliation by least squares

Parameter estimation by least squares

Economic optimization by standard methods


Plant model
Plant data
from DCS
Combined gross
error detection and
data reconciliation
Simultaneous data
reconciliation and
parameter estimation
Plant
economic
optimization
Optimal
setpoints
to DCS
Optimization
algorithm

Data Reconciliation

Adjust process data to satisfy material and energy balances.

Measurement error - **e**

$$\mathbf{e} = \mathbf{y} - \mathbf{x}$$

y = measured process variables
x = true values of the measured variables

$$\tilde{\mathbf{x}} = \mathbf{y} + \mathbf{a}$$

a - measurement adjustment

Data Reconciliation NLP

Measurements having only random errors - least squares

$$\underset{x}{\mathit{Minimize}}: \sum_{i=1}^{n} \left(\frac{y_i - x_i}{\sigma_i} \right)^2$$

$$\mathit{Subject\ to:} \quad f(x) = 0$$

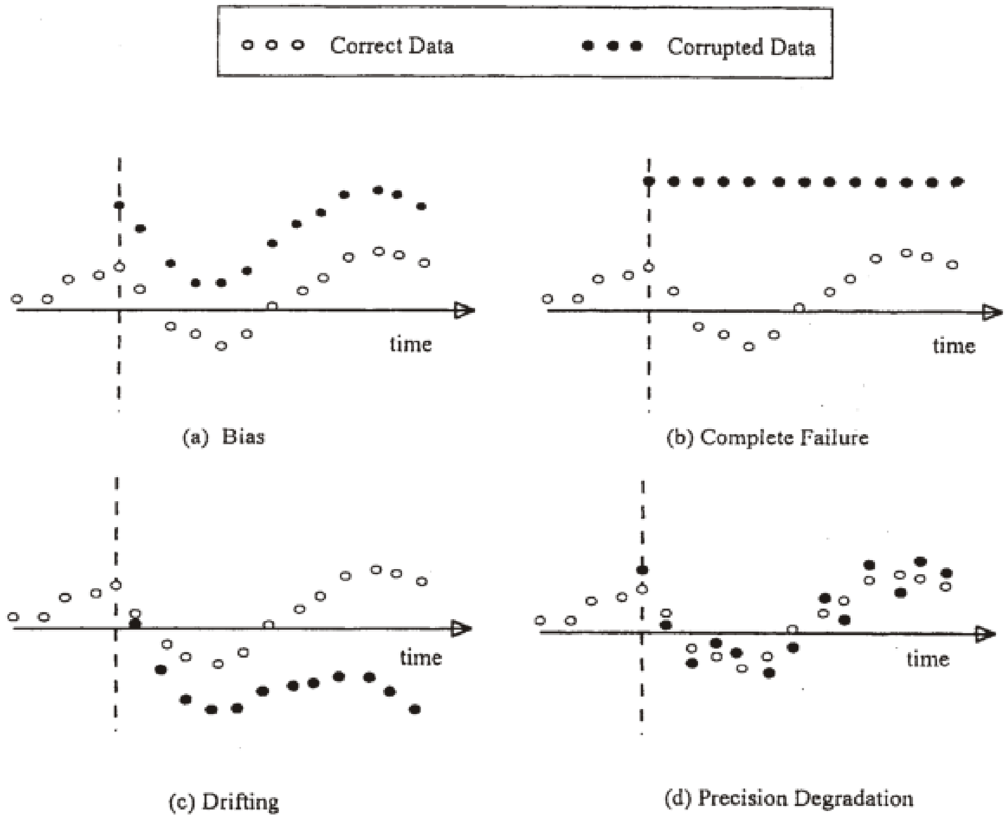
σ_i = standard deviation of y_i

f(x) - process model

- linear or nonlinear

Types of Gross Errors

Types of Gross Errors



Source: S. Narasimhan and C. Jordache, *Data Reconciliation and Gross Error Detection*, Gulf Publishing Company, Houston, TX (2000)

Gross Error Detection Methods

Statistical Testing

o many methods

o can include data reconciliation

Others

o principal component analysis

o ad hoc procedures – time series screening

Combined Gross Error Detection and Data Reconciliation

Measurement Test Method - least squares

$$\underset{\mathbf{x},\,\mathbf{z}}{\textit{Minimize}}: \quad (\mathbf{y} - \mathbf{x})^T\mathbf{Q}^{-1}(\mathbf{y} - \mathbf{x}) = \mathbf{e}^T\mathbf{Q}^{-1}\mathbf{e}$$

$$\textit{Subject to}: \quad \mathbf{f}(\mathbf{x}, \mathbf{z}, \theta) = 0$$

$$\mathbf{x}^L \leq \mathbf{x} \leq \mathbf{x}^U$$

$$\mathbf{z}^L \leq \mathbf{z} \leq \mathbf{z}^U$$

Test statistic:

if $|e_i|/\sigma_i \geq C$ measurement contains a gross error

Least squares is based on only random errors being present

Gross errors cause numerical difficulties

Need methods that are not sensitive to gross errors

Methods Insensitive to Gross Errors

Tjao-Biegler's Contaminated Gaussian Distribution

$$P(y_i \mid x_i) = (1-\eta)P(y_i \mid x_i, R) + \eta\, P(y_i \mid x_i, G)$$

$P(y_i \mid x_i, R)$ = probability distribution function for the random error

$P(y_i \mid x_i, G)$ = probability distribution function for the gross error.

$$P(y|x,G) = \frac{1}{\sqrt{2\pi}\, b\sigma}\, e^{\frac{-(y-x)^2}{2b^2\sigma^2}}$$

Results of Theoretical and Numerical Evaluation

Method based on contaminated Gaussian distribution had best performance for measurement containing random errors and gross errors in the range 3σ - 30σ.

Method based on Lorentzian distribution had best performance for measurement containing random errors and gross errors larger than 30σ.

Measurement test method had the best performance when only random errors were present. Significant error smearing (biased estimation) occurred for gross errors greater than 10σ.

Parameter Estimation
Error-in-Variables Method

Least squares

$$\underset{\boldsymbol{\theta}}{\mathit{Minimize}}: \quad (\mathbf{y}-\mathbf{x})^T\mathbf{Q}^{-1}(\mathbf{y}-\mathbf{x}) = \mathbf{e}^T\mathbf{Q}^{-1}\mathbf{e}$$

$$\mathit{Subject\ to}: \qquad \mathbf{f}(\mathbf{x}, \boldsymbol{\theta}) = 0$$

$\boldsymbol{\theta}$ - plant parameters

Simultaneous data reconciliation and parameter estimation

$$\underset{\mathbf{x},\, \boldsymbol{\theta}}{\mathit{Minimize}}: \quad (\mathbf{y}-\mathbf{x})^T\mathbf{Q}^{-1}(\mathbf{y}-\mathbf{x}) = \mathbf{e}^T\boldsymbol{\Sigma}^{-1}\mathbf{e}$$

$$\mathit{Subject\ to}: \qquad \mathbf{f}(\mathbf{x}, \boldsymbol{\theta}) = 0$$

another nonlinear programming problem

Three Similar Optimization Problems

Three Similar Optimization Problems

Optimize: **Objective function**
Subject to: **Constraints are the plant model**

Objective function

data reconciliation - distribution function
parameter estimation - least squares
economic optimization - profit function

Constraint equations

material and energy balances
chemical reaction rate equations
thermodynamic equilibrium relations
capacities of process units
demand for product
availability of raw materials

Interactive On-Line Optimization Program

1. Conduct combined gross error detection and data reconciliation to detect and rectify gross errors in plant data sampled from distributed control system using the Tjoa-Biegler's method (the contaminated Gaussian distribution) or robust method (Lorentzian distribution).

This step generates a set of measurements containing only random errors for parameter estimation.

2. Use this set of measurements for simultaneous parameter estimation and data reconciliation using the least squares method.

This step provides the updated parameters in the plant model for economic optimization.

3. Generate optimal set points for the distributed control system from the economic optimization using the updated plant and economic models.

Interactive On-Line Optimization Program

Process and economic models are entered as equations in a form similar to Fortran

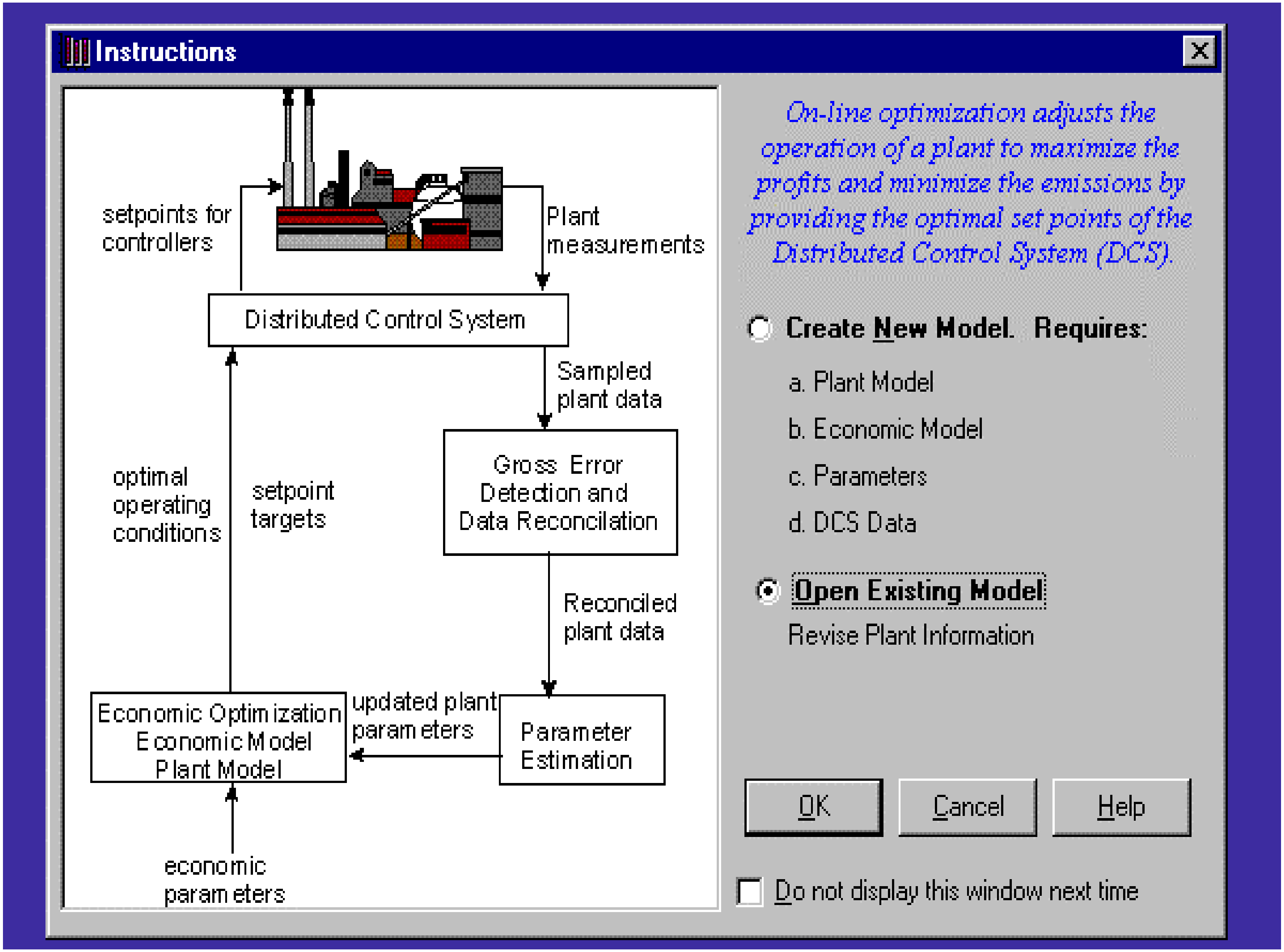
The program writes and runs three GAMS programs.

Results are presented in a summary form, on a process flowsheet and in the full GAMS output

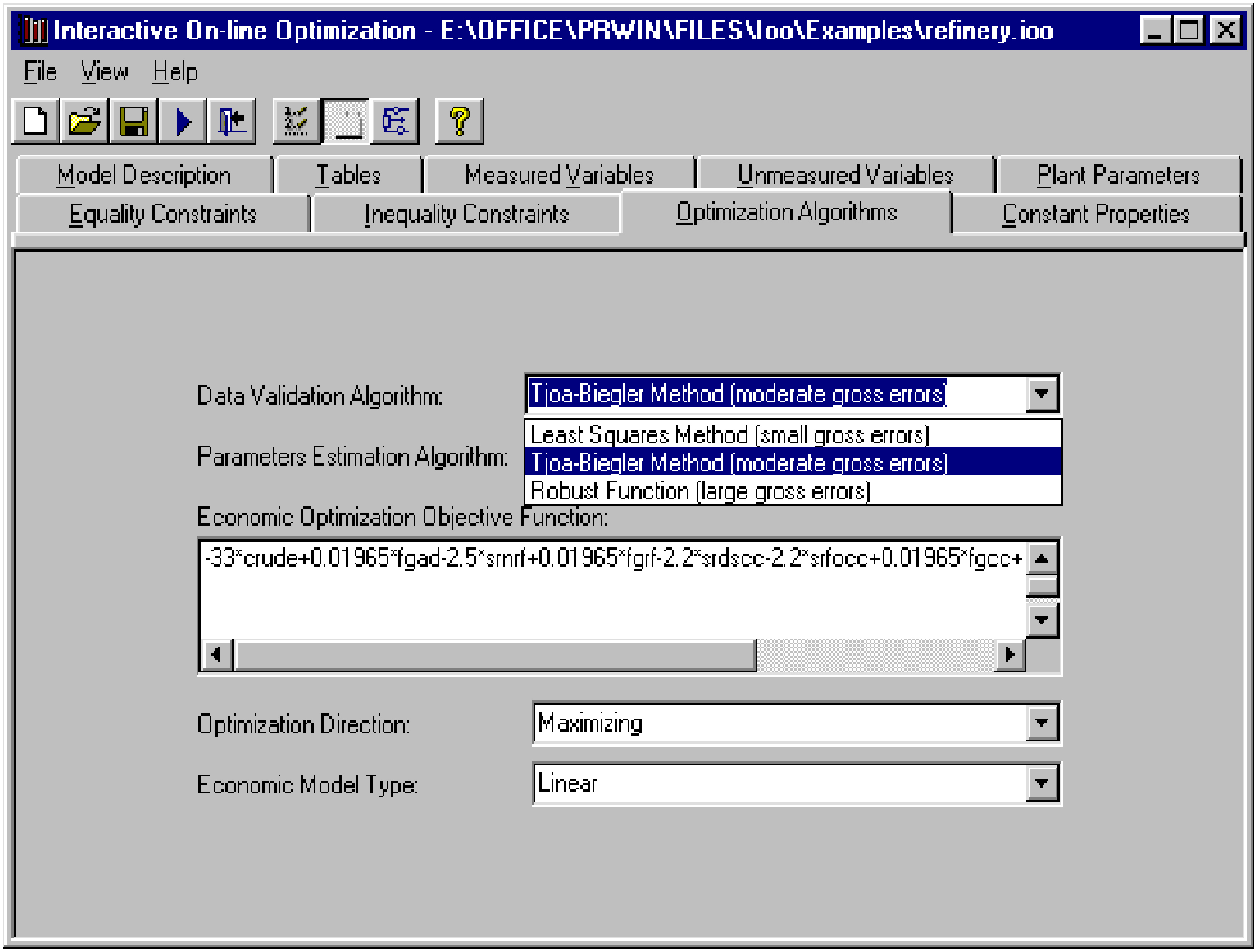
The program and users manual (120 pages) can be downloaded from the LSU Minerals Processing Research Institute web site

URLhttp://www.mpri.lsu.edu

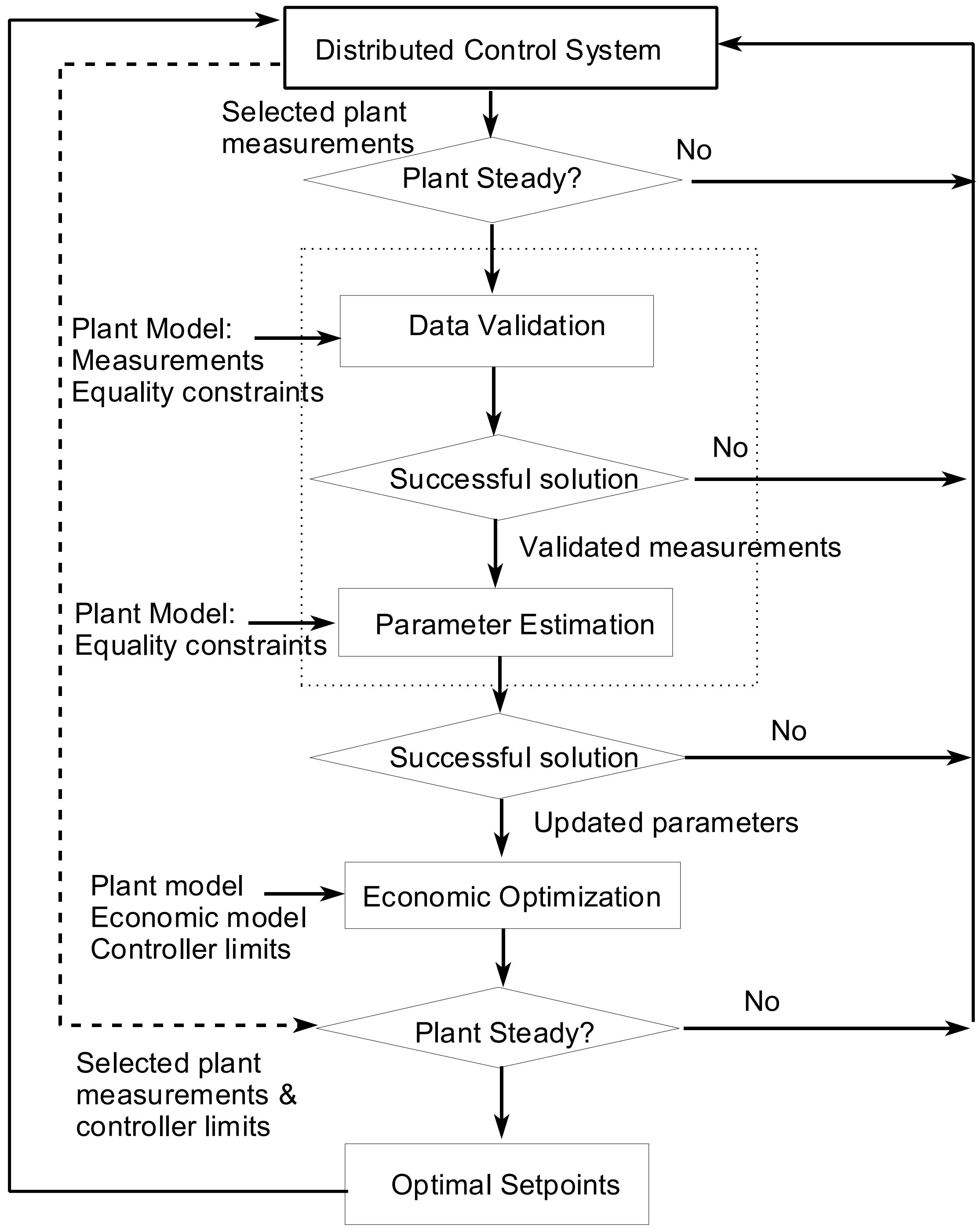
Opening Screen of On-Line Optimization Program



Algorithm Selection in On-Line optimization Program



Steady State Detection for On-Line Optimization



Some Other Considerations

Redundancy

Observeability

Variance estimation

Closing the loop

Dynamic data reconciliation
and parameter estimation

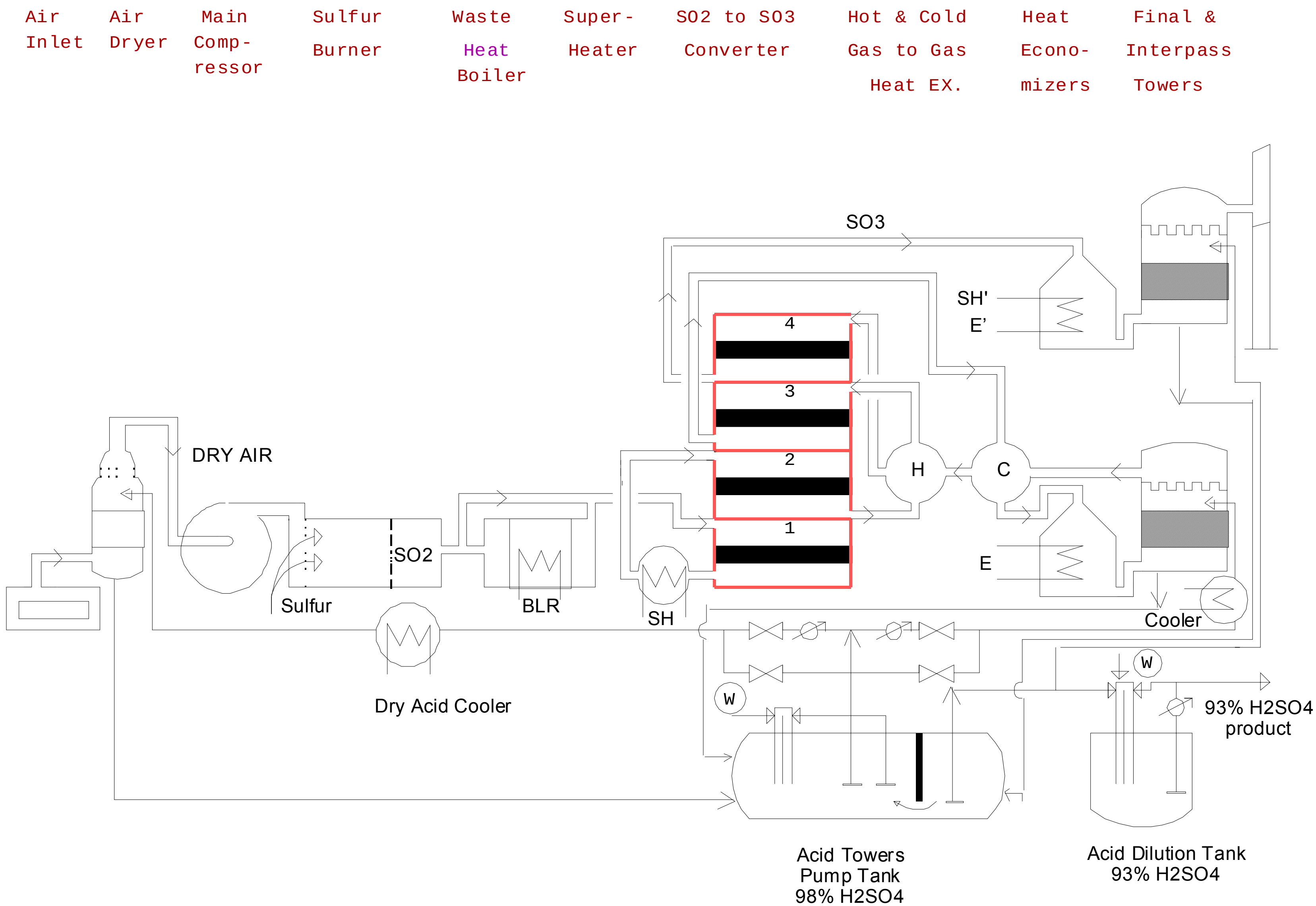
On-Line Optimization Summary

Summary

Most difficult part of on-line optimization is developing and validating the process and economic models.

Most valuable information obtained from on-line optimization is a more thorough understanding of the process

Process Flow Diagram for Contact Process



Validation of Contact Process Model

Table 4-14 The Comparison of Model Prediction and Plant Design Data for Convertor I

	Design Data	Model Prediction
FSO_2 $^{(In-Out)}$, Kmol/sec	0.337 - 0.129	0.337 - 0.129
FSO_3 $^{(In-Out)}$, Kmol/sec	0.007 - 0.215	0.007 - 0.215
FO_2 $^{(In-Out)}$, Kmol/sec	0.280 - 0.176	0.280 - 0.176
FN_2 $^{(In-Out)}$, Kmol/sec	2.373 - 2.373	2.373 - 2.373
Conversion of SO_2	62.5%	62.5%
Temp. (S06 - S07), K	693.2 - 890.2	692.5 - 890.9
Effectiveness factor	-	0.241

Contact Process Economic Optimization

Economic Optimization

Value Added Profit Function

$$s_{F64}F_{64} + s_{FS8}F_{S8} + s_{FS14}F_{S14} - c_{F50}F_{50} - c_{FS1}F_{S1} - c_{F65}F_{65}$$

On-Line Optimization Results

Date	Current ($/day)	Profit Optimal ($/day)	Improvement
6-10-97	37,290	38,146	2.3% $313,000/yr
6-12-97	36,988	38,111	3.1% $410,000/yr

Contact Process Potential Improvement

On-Line Optimization

Increased profit by 3%($350,000/yr)

Reduction in sulfur dioxide emissions by 10%

Improved understanding of the process

Alkylation

Isoparaffin-olefin alkylation produces branched paraffins in the gasoline range

Refineries use C_3 C_4 and C_5 hydrocarbon streams

Sulfuric acid catalyst concentration maintained above 88% to prevent polymerization

Reactor temperatures in the range of 10-20 ^oC

Alkylation is a two-phase system

- low solubility of isobutane in the catalyst phase
- intimate contact of the reactant and the catalyst
- efficient mixing with fine subdivision

Motiva Alkylation Process

15,000 BPD STRATCO Effluent Refrigerated Alkylation Plant

STRATCO reactor contacts the reactants in a high velocity propeller stream and removes heat from the exothermic reaction

Process flow diagrams

- prepared from P&ID's of the plant
- reaction section
- refrigeration, depropanizer and alkylate deisobutanizer sections
- saturate deisobutanizer section

Reactor Section

Four reactors

and acid settlers

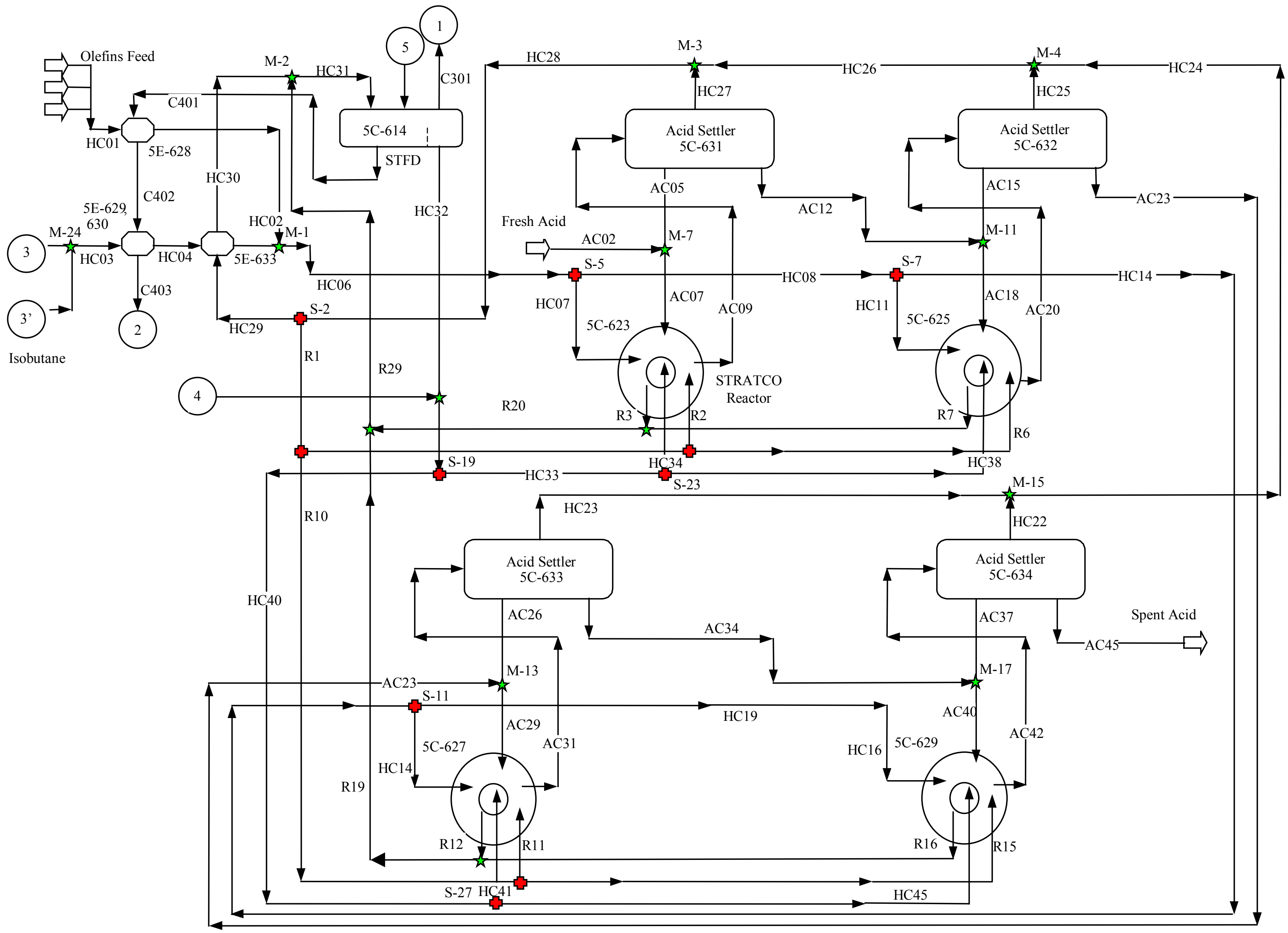
Three feed streams

Olefin feed (HC01)

Isobutane feed (HC03)

Recycled olefin/isobutane

(HC32)



Model Summary

Table 5.1. Summary of the Alkylation Process Model

Feature	Quantity
Process Units	76
Process Streams	110
Equality Constraints	1579
Inequality Constraints	50
Measured Variables	125
Unmeasured Variables	1509
Parameters	64

Model Validation

Establish accuracy of model to predict performance of plant

Used data validation

125 measured plant variables, 88 were within the accuracy of the measurements

Remaining 37 variables shown here with standard measurement error

ϵ_i ($\epsilon_i = |y_i - x_i|/\sigma_i$

Process engineers concluded that these 37 variables were within the range of possible process values

Model of the process accurately predicted its performance and can be used for on-line optimization.

Table 4.8. Plant vs. Model Data

Variable Name	Plant Data (y_i)	Reconciled Data from Data Validation (x_i)	Standard Measurement Error (ϵ_i)
FAC02	0.1125	0.1600	4.2235
FAC12	0.1259	0.1600	2.7085
FAC23	0.1253	0.1600	2.7653
FAC45	0.1040	0.1600	5.3846
FC308	2.1990	3.1032	4.1120
FC316	0.6581	1.8000	17.3515
FC322	0.4427	1.5619	25.2812
FC328	0.0942	0.0535	2.6399
FC403	3.8766	2.2834	4.1097
FC412	0.0324	0.0418	2.8968
FSC411	2.7287	1.3525	5.0436
FstmE612	0.1425	0.0889	3.7607
x1C417	0.0372	0.0255	3.1309
x2SC402	0.0136	0.0084	3.7929
x2SC408	0.0221	0.0002	9.9048
x3C325	0.0017	0.0000	10.0000
x3SC403	0.0103	0.0212	10.5665
x4C316	0.0580	0.0796	3.7155
x4SC408	0.0331	0.0088	7.3475
x5C316	0.0020	0.0060	19.8000
x5C417	0.0009	0.0295	286.2300
x5HC32	0.0096	0.0306	22.0134
x6SC402	0.0167	0.0666	29.8204
x6SC403	0.0250	0.0950	27.9946
x7HC32	0.0197	0.0497	15.2312
x7SC402	0.0022	0.0032	4.3956
x7SC408	0.0022	0.0000	10.0000
xx1C322	0.0027	0.1167	428.5338
xx1C414	0.0330	0.0800	14.2498
xx2HC01	0.4525	0.1291	7.1481
xx3C407	0.0003	0.0000	7.4194
xx3HC01	0.3558	0.0125	9.6498
xx4C407	0.1124	0.0853	2.4068
xx5C407	0.0803	0.1506	8.7555
xx5C412	0.0022	0.0581	255.6751
xx5C414	0.0021	0.0011	4.8325
xx7C414	0.0015	0.0080	44.4218

Alkylation Process Economic Model

Profit = Sales - Cost – Utilities

Sales = Alkylate (C_3, C_4 and C_4 Raffinate) produced * Price of alkylate

Cost = Σ Input * Cost

Utilities = Σ Input * Utility Cost

Raw Material/Utility Costs and Product Prices

Table 5.4. Alkylation Plant Raw Material/Utility Costs and Product Prices

Feed and Product	Stream Number	Cost and Price ($/bbl) Summer	Winter
Feeds			
Propylene	HC01	11.79	10.44
Butylene	HC01	18.00	16.56
Iso-butane	SC414	16.88	17.39
Products			
N-butane	SC405, C413	13.29	12.71
C_3 Alkylate	C407	24.49	22.30
C_4 Alkylate	C407	26.32	24.06
C_4 Raffinate Alkylate	C407	26.34	24.19

Catalyst and Utilities	Cost
H_2SO_4(Stream AC02)	$110/Ton
Electricity	$0.04/KWH
50# Steam	$2.50/M-Lbs
250# Steam	$3.60/M-Lbs
600# Steam	$4.40/M-Lbs

On-Line Optimization

Process Data from Distributed Control System

Plant measurement at 1.0 minute intervals over a two day period

Six steady state periods identified using time series with MathCAD graphics

Data Reconciliation and Gross Error Detection

Robust Lorentzian function method and CONOPT2

Optimal solution obtained in 1,200 iterations

Reconciled measurements reported and about 30 gross errors identified

Parameter Estimation and Data Reconciliation

Optimal solution obtained in 1,500 iterations

Small adjustments in values of parameters

On-Line Optimization Results Economic Optimization

Table 5.5. Calculated Profit after Data Validation (D.V.), Parameter Estimation (P.E.) and Economic Optimization (E.O.) Steps for six Different Operation Points (Steady States)

Operation points	**D.V.**	**P.E.**	**E.O**	**% Increase**
#1	11.9	12.1	29.1	144
#2	7.4	7.4	21.4	189
#3	21.4	22.1	26.9	26
#4	7.0	7.0	22.1	216
#5	10.1	23.3	26.3	160
#6	22.0	23.6	27.6	25
			Average % increase	127

Improvement in profit

8.5% reduction in costs and 2.2% increase in sales

5.5% more olefin charge

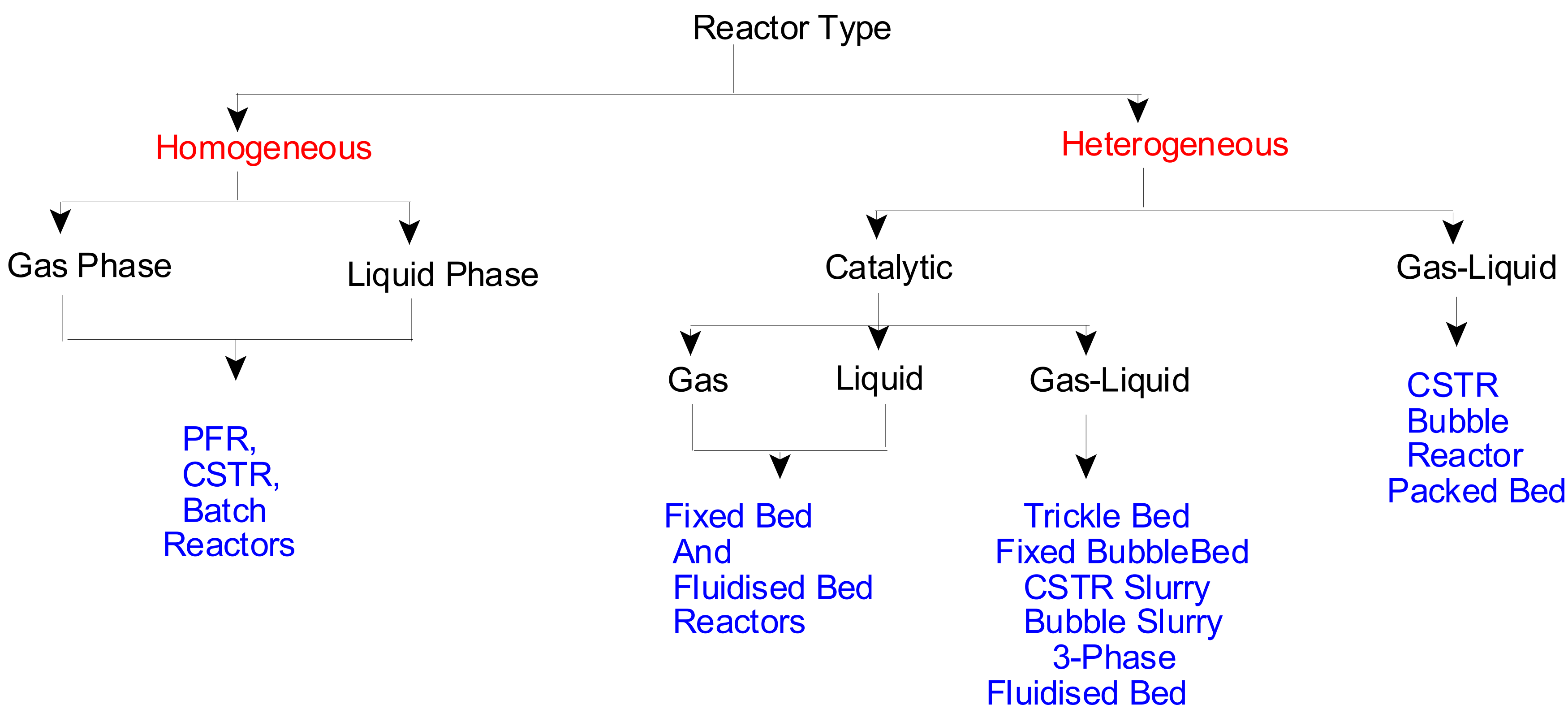
98% reduction in isobutane purchase cost (because of reduced isobutane flow rate)

7.2% reduction in saturate feed to the Saturate Deisobutanizer column

2.2% increase in the alkylate (alkylate quality did not change at optimal operation)

Average of 9.4×10^9 BTU/yr in energy savings from steam usage in the distillation columns

Reactor Analysis



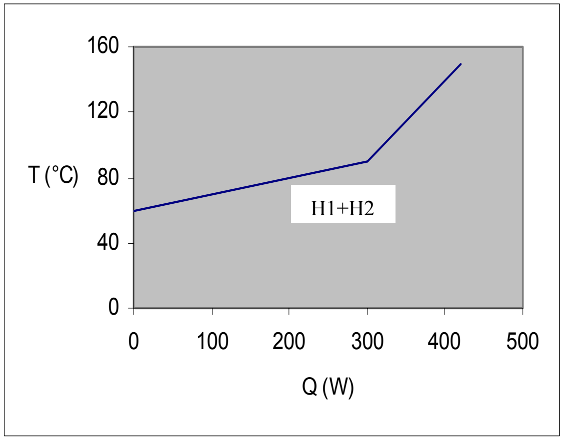
Contact Process Chemical Reactor Improvement

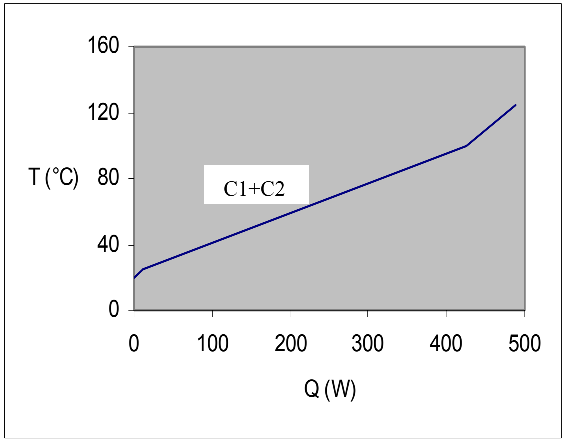
Chemical Reactor Analysis

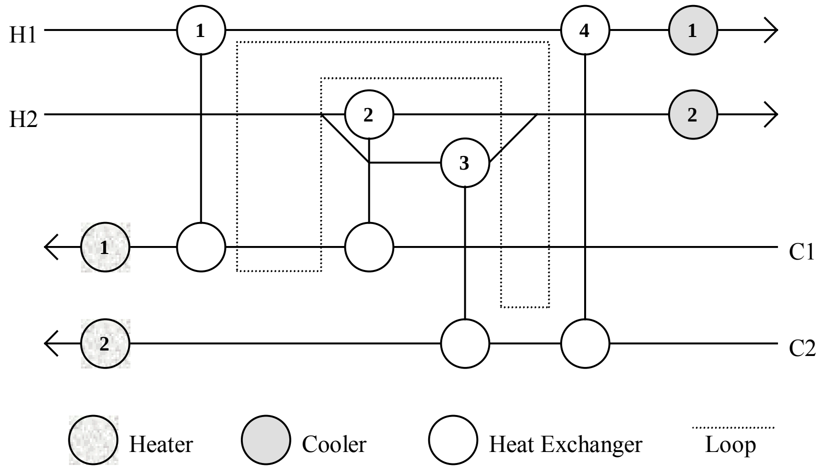
Conversion could be increased by 19% in the first reactor.

Reactor volumes could be reduced by 87% by using a reactor pressure of 10.3 atms rather than current operations at 1.3 atms.

Energy Integration – Pinch Analysis







Contact Process Pinch Analysis

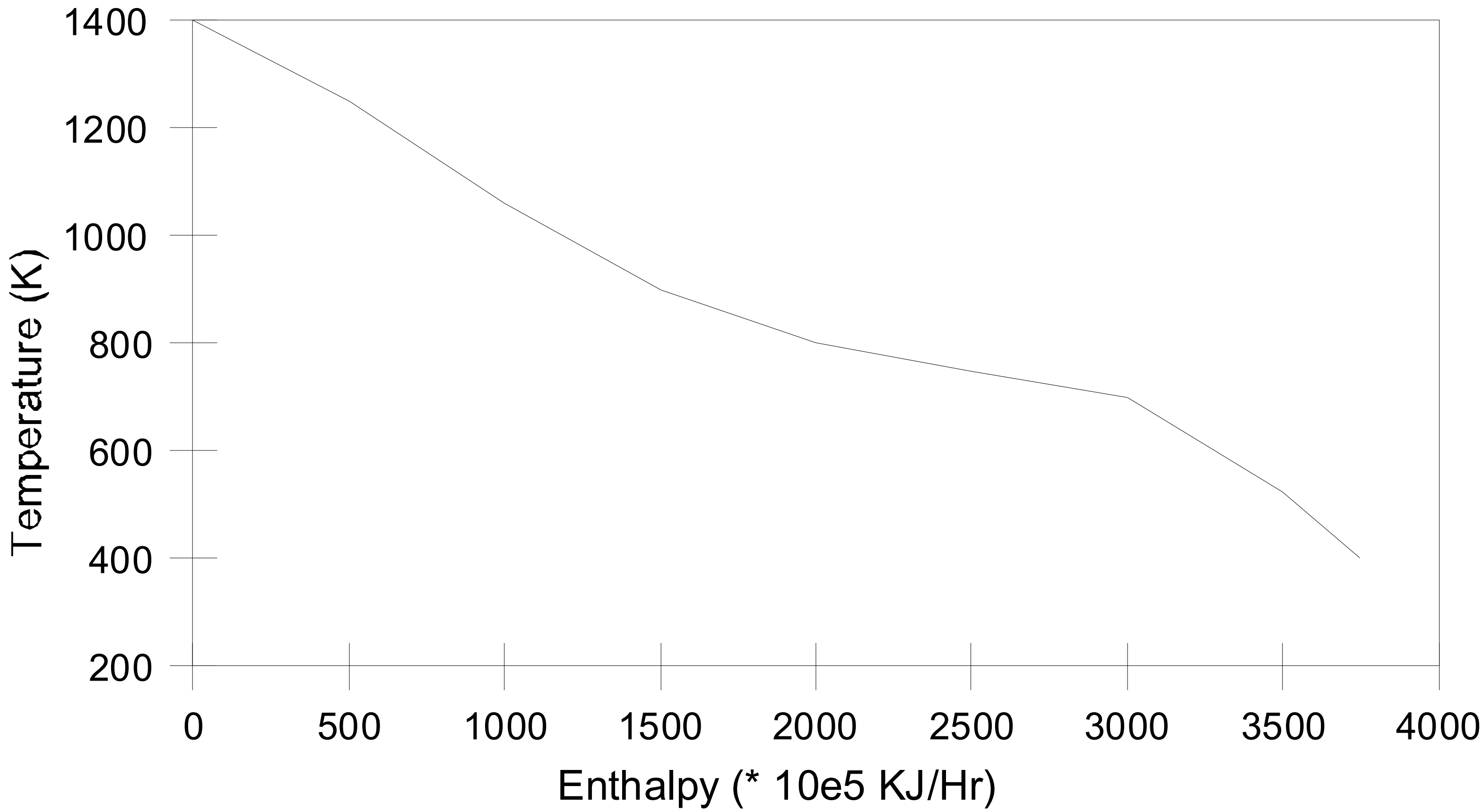


Fig. 5 Grand Composite Curve for the Contact Process

Contact Process Pinch Analysis

Process is below the pinch, and no hot utilities are required.

A proposed heat exchanger network has 25% less area than the current one.

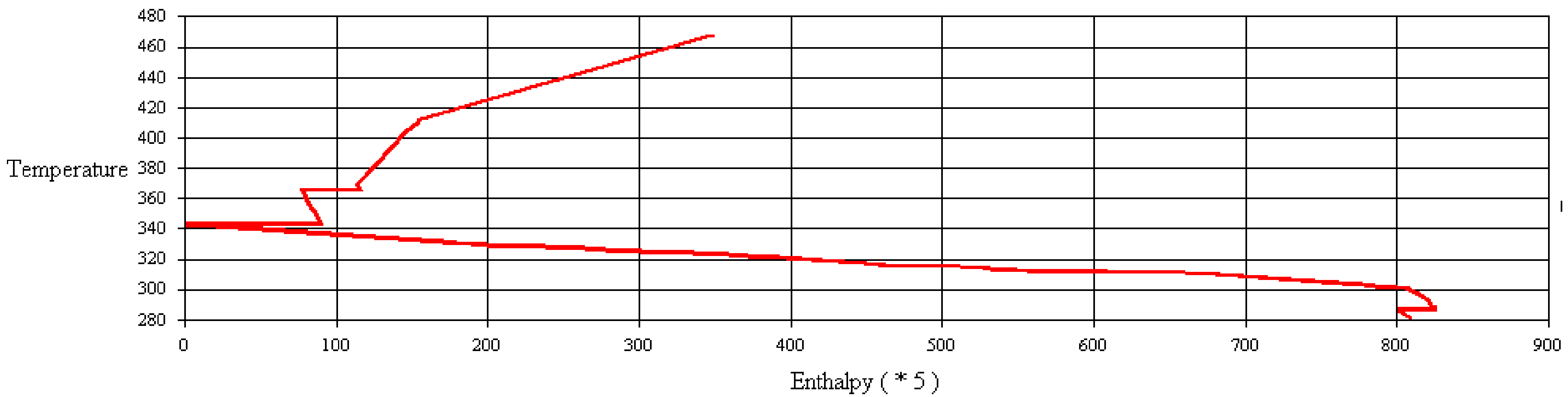
Energy Integration – Pinch Analysis

Alkylation process is very energy intensive

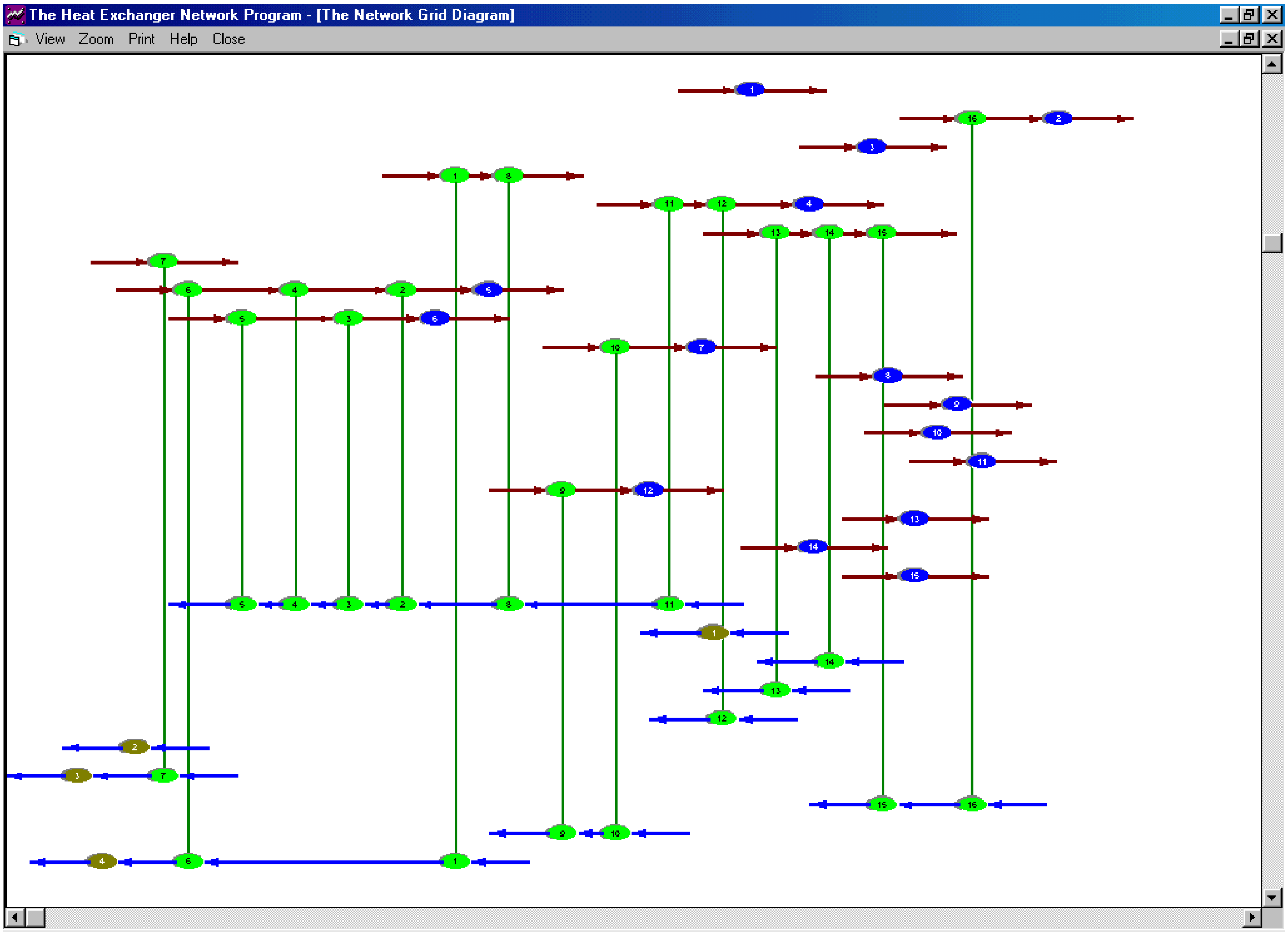
Alkylation process model has 28 heat exchangers, plus four contactors. Heat exchange in contactors not included in the pinch analysis

Grand Composite Curve

End points of the curve gives the minimum values of external heating and cooling required by the process



Pinch Analysis – Maximum Energy Recovery Network Diagram



Pinch Analysis – Minimum Utilities

Minimum Utilities

1742 MJ/min steam (external heat)

4043 MJ/min of cooling water (external cooling)

Current Operations

1907 MJ/min steam (external heat)

4300 MJ/min of cooling water (external cooling)

Pinch Analysis – Optimum Heat Exchanger Configuration

Current Configuration

6 heat exchangers, 4 heaters and 12 coolers

Optimal Configuration

16 heat exchangers, 4 heaters and 15 coolers

Additional heat exchangers reduce energy requirements

May result in operational difficulties

See report for pressure shift applied to distillation columns

Pollution Assessment

Assess the pollutants generated in the process

Determine location of generation

Modify process for waste minimization

Contact Process Pollution Assessment

Process units identified for modification to reduce sulfur dioxide emissions were the sulfur furnace and the four packed bed reactors

Pollution Assessment

Waste Reduction Algorithm (WAR) and

Environmental Impact Theory

Pollution Index

I = wastes/products = - (ΣOut + ΣFugitive) / ΣP_n

Potential Environmental Impact

$$\Psi_k = \sum_l \alpha_l \Psi^s_{k,l}$$

α_l relative weighting factor

$\Psi^s_{k,l}$ units of potential environmental impact/mass of chemical k

$\Psi^{s}_{k,l}$ Values used in Alkylation Process Model

Component	Ecotoxicity (aquatic)	Ecotoxicity (terrestrial)	Human Toxicity (air)	Human Toxicity (water)	Human Toxicity (soil)	Photochemical Oxidant Formation
C_3-	0.0305	0	9.06E-7	0	0	1.1764
C_4=	0.0412	0.3012	0	0.3012	0.3012	1.6460
iC_4	0.1566	0.2908	8.58E-7	0.2908	0.2908	0.6473
nC_4	0.1890	0.2908	8.58E-7	0.2908	0.2908	0.8425
iC_5	0.0649	0.2342	0	0.2342	0.2342	0.6082
nC_5	0.3422	0.2342	5.53E-7	0.2342	0.2342	0.8384
iC_6	0.2827	0.1611	0	0.1611	0.1611	1.022
H_2SO_4	0.0170	0.1640	0.2950	0.1640	0.1640	0

Source EPA National Laboratory for Sustainable Development

Pollution Assessment

Table 5.6. Input and Output Streams in Alkylation Process.

Stream	Description	Type	Pollution Index
AC02	Fresh Acid Feed	Input	0.808
HC01	Olefin Feed	Input	1.622
SC414	Make-up Isobutane	Input	1.611
SC401	Sat-Deisobutanizer Feed	Input	1.789
AC45	Spent Acid	Non-Product	1.034
C320	To LPG Storage	Product	0
C328	To Fuel Gas	Product	0
C407	To Alkylate Storage	Product	0
C413	To N-butane Storage	Product	0
SC405	To N-butane Storage	Product	0

Pollution Assessment before and after Economic Optimization

Program calculates pollution indices for each input, produce and non-product stream in the process

These values are used to calculate the six pollution indices for the process

Negative values mean that the input streams are actually more harmful to the environment than the non-products if they are not processed through the alkylation process

Table 5.7. Pollution Assessment Values (BEO) and after (AEO)

Index Type	Value (BEO)	Value (AEO)	
Total rate of impact generation	**-4.9120**	**-4.7966**	**impact/time**
Specific impact generation	-3.2860	-3.4584	impact/product
Pollution generation per unit product	-0.9777	-0.9742	mass of pollutant/mass of product
Total rate of impact emission	1.0325	1.0337	impact/time
Specific impact emission	0.6897	0.7453	impact/product
Pollutant emission per unit product	0.1069	0.1154	mass of pollutant/mass of product

Conclusions – Flowsheeting

Demonstrated Capability of Advanced Process Analysis System

- process flowsheeting
- on-line optimization
- pinch analysis
- pollution assessment
- chemical reaction analysis determined best alkylation reaction kinetics

Process Flowsheeting

76 process units, 110 process streams

1,579 equality, 50 inequality constraints, 1,634 variables

Simulation validated using plant data and data reconciliation

Simulation predicted the performance of the plant within the accuracy of the data

Conclusions – Economic Optimization

Evaluated six operating points

25% to 215% increase in the profit

Increase of 145% included

- 8.5% reduction in costs and 2.2% increase in sales
- 5.5% more olefin charge
- 98% reduction in isobutane purchase cost
- 7.2% reduction in feed to the Sat Deisobutanizer
- 2.2% increase in the alkylate
- 2.2% reduction in the sulfuric acid consumption.
- 1.0% reduction in energy to 1888 MJ/min

Conclusions – Pinch Analysis and Pollution Assessment

Pinch Analysis

7.7% reduction in steam to 67×10^9 BTU/yr

6.0% reduction in cooling water to 106×10^9 BTU/yr

Pollution Assessment

Demonstrated ability to locate and estimate the severity pollutant emissions from the process.

Conclusions - Summary

Development and validation of process simulation

most difficult and time consuming part

of applying the System

Applicable to small plants

Typical improvements

5% for on-line optimization

5 –35% for pinch analysis

Detailed understanding of process

- most valuable result
- difficult to measure value

Program and users manual downloaded from

‘www.mpri.lsu.edu - no charge